

# Phase II Tungsten Fate-and-Transport Study for Camp Edwards

Jay L. Clausen, A. Bednar, D. Lambert, R. Bailey, M. Kuhlbrush, S. Taylor, and S. Bigl

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<sup>1</sup>Cold Regions Research and Engineering Laboratory U.S. Army Engineer Research and Development Center 72 Lyme Road Hanover, NH 03755-1290

<sup>2</sup>Environmnetal Laboratory U.S. Army Engineer Research and Development Center 3909 Halls Ferry Road Vicksburg, MS 39180-6199

<sup>3</sup>U.S. Army Corps of Engineers 696 Virginia Road New England District Concord, MA 01742-2751

#### Final report

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**Abstract:** Tungsten was detected in soil and groundwater beneath the Bravo Small Arms Range (SAR) at Camp Edwards, Massachusetts. This discovery prompted additional studies to assess tungsten's fate-and-transport. Installation of drive points and groundwater monitoring wells at three SARs [Bravo (B), Charlie (C), and South East/South West] indicate that groundwater contamination is restricted to B Range. Although tungsten is still present in groundwater monitoring well MW-72S at Bravo Range, concentrations have dropped significantly since the removal of soil and have stabilized at a less than 2  $\mu$ g/L concentration. Soil remediation consisted of removal of all berm soil that contained tungsten with a level greater than 150 mg/kg. Similarly, shallow lysimeters installed at B, C, and India Ranges also indicate a decline in tungsten levels post-soil removal. Deep lysimeters at B range, installed after soil removal activity, indicate that tungsten is present in pore water at least 7.6 meters below ground surface.

Batch and column laboratory studies performed as a part of this program demonstrated that tungsten metal in contact with water readily releases dissolved species, and soil partition coefficients (K<sub>d</sub>) do not stabilize in batch studies for 30 to 60 days. The K<sub>d</sub> values are highly variable, range from 18 to 477 L/kg, and are dependent upon the length of contact time. The rate of dissolution from a tungsten particle appears to range from 0.022 to 0.067 mg/day. These findings indicate that metallic tungsten and tungsten oxides are rapidly dissolved under high-intensity precipitation events and are transmitted through the vadose zone soils as tungstate and polytungstate species. In contrast, under low-precipitation intensity events, the rates of dissolution and infiltration are lower, resulting in a greater degree of tungstate and polytungstate sorption. Consequently, the release pattern of tungsten in the aquifer at Camp Edwards will be in a slug- or pulse-type fashion and dependent on infiltration rates. Thus, a contiguous area of groundwater contamination is not expected. Additionally, the capacity for Camp Edwards soils to adsorb tungstate is high. If tungstate reaches groundwater, it will continue to be adsorbed by the aquifer matrix, resulting in limited migration from the source area.

Preliminary water speciation studies indicate that the presence of tungsten to a depth of 4.6 m in the vadose zone is comprised of tungstate and polytungstate species, indicating the polymerization of tungstate. Tungstate, however, is the only species found in groundwater. Polytungstate migra-

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tion is seemingly attenuated by adsorption processes that prevent it from reaching groundwater.

Conventional  $K_d$  modeling approaches seriously under predict tungsten migration at Camp Edwards SARs. Clearly, factors that control tungsten mobility are not included in these models. Importantly, soil geochemical conditions, such as redox potential and pH, affect tungsten speciation and its interaction with the subsurface. More research is required to determine the exact mechanisms responsible for tungsten migration at SARs, but data from this study suggest that implemented remedial actions at Camp Edwards have significantly limited the potential for widespread contamination from use of tungsten training rounds.

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## **Nomenclature**

ASTM American Society of Testing Methods

bgs below ground surface

bwt below water table

CRREL Cold Regions Research and Engineering Laboratory

DI deionized water

**ECC** Environmental Chemical Corporation

EL Environmental Laboratory

EMC Environmental Management Commission

ERDC U.S. Army Engineer Research and Development

Center

HPLC/ICP/MS high performance liquid chromatography/inductively

coupled plasma/mass spectrometry

IAGWSP Impact Area Groundwater Study Program

ICP-MS inductively-coupled plasma mass spectrometry

K<sub>d</sub> soil/water partitioning coefficient

MAARNG Massachusetts Army National Guard

MADEP Massachusetts Department of Environmental

**Protection** 

MMR Massachusetts Military Reservation

CENAE U.S. Army Corps of Engineers – New England District

NAU Northern Arizona University

rpm revolutions per minute

SAR small arms range

SVOC semi-volatile organic compound

STL Severn Trent Laboratory (now Test America)

USACE U.S. Army Corps of Engineers

USAEC U.S. Army Environmental Command

USEPA U.S. Environmental Protection Agency

USGS U.S. Geological Survey

 $WO_4^{2-}$  tungstate

XAS synchrotron-based x-ray absorption spectroscopy

## **Preface**

This report was prepared by Jay L. Clausen, Dennis Lambert, Ronald Bailey, Susan Taylor and Sue Bigl, Biogeochemical Sciences Branch (BSB), U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire. Additional authors include Anthony Bednar, Environmental Chemistry Branch, Environmental Laboratory (EL), ERDC, Vicksburg, Mississippi, and Michael Kuhlbrush, U.S. Army Corps of Engineers, New England District, Concord, Massachusetts.

The U.S. Army Environmental Command provided funding for this work. Alan Hewitt and Dr. Terrance Sobecki, CRREL, provided technical reviews.

This report was prepared under the general supervision of Terrence Sobecki, Branch Chief, BSB, CRREL; Dr. Justin Berman, Chief, Research and Engineering Division, CRREL; and Dr. Robert E. Davis, Director, CRREL. The Commander and Director of the ERDC is Col. Gary E. Johnston. The Director is Dr. Jeff Holland.

## **Unit Conversion Factors**

Multiply	Ву	To Obtain
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
degrees Fahrenheit	(°F-32)/1.8	degrees Celsius (°C)
feet	0.3048	meters
gallons (U.S. liquid)	3.785412 E-03	liters
inches	0.0254	meters
pounds (mass)	0.45359237	kilograms
pounds (mass) per cubic foot	16.01846	kilograms per cubic meter

## 1 Introduction

The U.S. Army Corps of Engineers, Environmental Research and Development Center (ERDC), Cold Regions Research Engineering Laboratory (CRREL), Hanover, NH, was tasked by the U.S. Army Environmental Command (USAEC) to assess fate-and-transport properties of tungsten that has leached from tungsten/nylon bullets. The tungsten/nylon bullet was developed by the U.S. Army as a more environmentally-friendly replacement for the lead bullet (SERDP 1997). Metallic tungsten was considered environmentally benign because researchers believed it was essentially insoluble, with little or no mobility in soil and water. However, previous studies at the Massachusetts Military Reservation (MMR) at Camp Edwards demonstrated that metallic tungsten used in these projectiles was mobile under some conditions (Clausen et al. 2007a, b).

Prior to 2000, the environmental fate of tungsten had not been examined in much detail because of a lack of suitable analytical techniques and a general belief that tungsten was relatively insoluble and inert. This belief persisted even though metallurgical literature had suggested tungsten might be relatively soluble under appropriate conditions of pH and redox potential (Osseo-Asare 1982).

We are now aware that intact (or partially intact) bullet fragments deposited in metallic form can be chemically oxidized into soluble ions, which are subject to leaching with percolating water. Under oxidizing conditions, the stable and soluble forms of tungsten are tungstate ( $WO_4^{2-}$ ) or oxide complexes in the +6 oxidation state. The study of tungsten's environmental behavior is complicated by its propensity to polymerize; reactions favored at lower pH and higher tungsten concentrations. The oxidizing and relatively low pH soil environment at Camp Edwards is favorable for the formation of tungstate and polytungstates (Dermatas et al. 2004; Koutsospyros et al. 2006).

Several recent studies have discussed tungsten mobility in the environment. These include corrosion of tungsten and its alloys under environmental conditions (Ogundipe et al. 2004), bioaccumulation in plants (Wilson and Pyatt 2006), toxicity to bacteria and plant species (Strigul et al. 2005), and migration through the vadose zone of a sandy soil (Clausen and

Korte, in review). Because soluble forms are typically anionic, the environmental behavior of tungsten is distinctly different than most other metal contaminants (lead, copper, and zinc) associated with military small arms ranges (SARs). For example, phosphate has been added to training ranges to limit lead migration by formation of insoluble lead phosphates (Bricka et al. 2004) at Camp Edwards. In contrast, laboratory data (Xu et al. 2006) suggest phosphate and tungstate will compete for adsorption sites or react to form soluble complexes. Addition of phosphate, while it fixates lead, may enhance tungsten mobility. In addition, Bednar et al. (2008) found that tungstate polymerization occurs over time and apparently decreases mobility. However, these researchers noted a lack of precise definition of exact species and their stability.

Camp Edwards was chosen as a tungsten study site because tung-sten/nylon projectiles have been fired there since October 1999, and detailed records are available regarding the number of bullets fired per range (Clausen et al. 2007a, b). The initial study reported levels of tungsten in soil and soil pore water at three evaluated ranges (Bravo (B), Charlie (C), and India (I) Ranges). Tungsten concentrations in surface soils ranged as high as 2,080 mg/kg. Samples from lysimeters installed into range berms showed tungsten levels in the soil pore water up to 400 mg/L. Samples from monitoring well MW-72S, located approximately 10 m downgradient of the berm on B Range, contained tungsten at levels between 0.005 and 0.560 mg/L. These findings raised concerns that tungsten was migrating away from the SAR and could affect downgradient water supplies.

This report describes supplemental laboratory experiments and fieldwork assessing the fate-and-transport of tungsten at Camp Edwards SARs. Information is provided to assist the following organizations in future decisions regarding tungsten's environmental behavior: the U.S. Army, U.S. Army Environmental Command (USAEC), Impact Area Groundwater Study Program (IAGWSP), and Massachusetts Army National Guard (MAARNG). The information should also be valuable to organizations providing oversight or regulation for sites where tungsten has been used; e.g. the U.S. Environmental Protection Agency (USEPA), Massachusetts Department of Environmental Protection (MADEP), and the Environmental Management Commission (EMC).

The project team included:

 Technical Representative and Program Manager - Kimberly Watts (USAEC)

- Technical Project Manager Dr. Bonnie Packer (USAEC)
- Principal Investigator Jay Clausen (ERDC-CRREL)
- Field Coordinator John Ehret (U.S. Army Corps of Engineers (USACE) New England District (CENAE)

All field activities were coordinated through John Ehret at the USACE—CENAE. Mr. Ehret was responsible for communicating with the Camp Edwards IAGWSP, coordinating with Massachusetts Military Reservation (MMR) subcontractors and informing Jay Clausen of any changes in field activities. Jay Clausen was responsible for communication with Kimberly Watts and Bonnie Packer of USAEC.

## 2 Objectives

Based on Phase I study efforts (Clausen et al. 2007a, b), the primary objective of this project was to further describe and explain the fate-and-transport of tungsten in the environment. The secondary objective was to determine the extent of tungsten migration from surface soils to ground-water at Camp Edwards by installing and sampling drive points, ground-water wells, and lysimeters. Evidence from one well, MW-72S on B Range, already demonstrated that tungsten migrated to the aquifer in less than 6 years. Drive points and groundwater wells installed for this work have the ancillary purpose of aiding the IAGWSP to further understand flow paths for both pore water and ground water at the SAR.

A third objective was to determine how quickly tungsten metal in tung-sten/nylon bullets dissolved and moved through the soil. The degree of dissolution, sorption, and desorption was measured in drip experiments, standard batch tests, and column studies. Speciation of tungsten in water was examined with high performance liquid chromatography/inductively coupled plasma/mass spectrometry (HPLC/ICP/MS). Because tungsten can exist in multiple oxidation states and its speciation is poorly known, laboratory x-ray absorption spectroscopy is being used to identify and quantify the physical and chemical forms of tungsten in Camp Edwards soil cores. The soil speciation work was completed in February 2009 and documented in a supplemental addendum to this document.

The Phase II Study was divided into a series of tasks:

- Task 1. Prepare Work Plan (Clausen 2006).
- Task 2. Collect groundwater drive-point samples from several locations downgradient of the SARs (B and SE/SW Ranges) and install monitoring wells (B, C, and SE/SW Ranges) to assess the nature and extent of tungsten contamination.
- Task 3. Install lysimeter clusters at depths of 1.5, 4.6, and 7.6 m (5, 15, and 25 ft) bgs at one location at the B Range to assess the unsaturated zone transport of tungsten.

• Task 4. Determine tungsten dissolution rates from tungsten/nylon material via drip tests and with batch and column studies.

- Task 5. Perform adsorption/desorption laboratory batch and column studies to quantify the interaction of tungsten and lead with Maectitetreated surface soils, untreated surface soils, and subsurface soils under a variety of conditions.
- Task 6. Perform unsaturated zone modeling using data from Tasks 2, 3, and 4 to predict the rate of tungsten transport across the entire unsaturated zone; i.e. approximately 36 m (120 ft).
- Task 7. Perform groundwater modeling using data from Tasks 2 through 6 to determine the tungsten transport rate and the predicted extent in the saturated zone for all 12 SARs at Camp Edwards.
- Task 8. Determine the species of tungsten present in the environment (to be provided in an addendum report).
- Task 9. Complete Interim and Final Reports (this document) and perform project management and routine reporting tasks as appropriate.

## **3 Water Sampling and Analysis Methods**

Water samples from the monitoring wells were collected in 500-mL plastic bottles by the Environmental Chemical Corporation (ECC), a contractor working for the CENAE on behalf of the IAGWSP. Four samples were collected from each well: 1) unfiltered and unpreserved; 2) unfiltered and preserved; 3) filtered and unpreserved; and 4) filtered and preserved. Samples were filtered in the field using an inline 0.45-µm filter. Preserved samples were collected in pre-acidified sample bottles containing nitric acid. All samples were then chilled to 4°C and shipped to the respective laboratory. Sample splits were provided to ERDC-Environmental Laboratory (EL) and Dr. Ketterer at Northern Arizona University (NAU). Drivepoint samples and lysimeter samples for this study were collected without acid preservation, according to procedures for tungsten as previously described by Clausen et al. (2007a, b).

Water samples were tested for tungsten at ERDC-EL and NAU using inductively-coupled plasma mass spectrometry (ICP-MS) according to U.S. Environmental Protection Laboratory (USEPA) Method 6020. Samples were prepared according to USEPA Method 3050 with some modifications (Clausen et al. 2007b). Method 3050 typically involves preserving the water sample by adding a small volume of acid. However, acidification can influence tungsten solubility and speciation. Using concentrated acid is especially problematic when determining tungsten concentrations, because acids can form insoluble tungstates and polytungstates. Therefore, ERDC's procedure for tungsten analysis does not include field preservation with acid. Samples are simply chilled to 4°C and analyzed as soon as possible. For those samples not preserved upon collection, both NAU and ERDC-EL acidify the sample aliquot with nitric acid immediately prior to injection into the ICP-MS. This acidification stabilizes the other metals present so they can be assessed along with tungsten. The brief period of acid contact with tungsten prior to analysis is insufficient to cause formation of any insoluble tungstates and polytungstates.

During Phase I of the Tungsten SAR Study, many of the samples from lysimeters and monitoring wells were split and sent to both ERDC-EL and NAU for analysis. Evaluation of the data reported by Clausen et al. (2007b; Appendix A) demonstrated good agreement between these two independ-

ent laboratories. Consequently, a high degree of confidence exists in reporting tungsten concentrations as low as  $1 \,\mu\text{g/L}$ .

The reporting limit for tungsten ranged from 1 to 15  $\mu$ g/L, with a detection limit of about.2  $\mu$ g/L for the Severn Trent Laboratory (STL), and 0.3 to 0.8  $\mu$ g/L for ERDC-EL and NAU. Detection and reporting limits vary between sample runs because of differences in calibration as well as matrix interferences. In addition to testing for tungsten, ERDC-EL analyzed samples for antimony, arsenic, chromium, copper, iron, lead, manganese, molybdenum, nickel, selenium, vanadium, and zinc. Details on analysis and preparations performed by NAU and ERDC-EL are found in Clausen et al. (2007b).

## **4.0 Results and Discussion**

#### 4.1 Task 2 – Groundwater evaluation

#### 4.1.1 Historical perspective – summarized Phase I groundwater results

During Phase I, water samples were collected four times from four monitoring wells (Appendix A) and analyzed for tungsten by two independent laboratories – ERDC-EL and NAU. Both laboratories reported similar tungsten concentrations for all samples (Clausen et al. 2007b).

Two of the monitoring wells were located downgradient of SARs where tungsten rounds had been fired (MW-72S and MW-123S), and two wells (MW-135M2 and MW-404S) were selected to evaluate the background concentration. One down-gradient well, MW-123, had no tungsten above the reporting limit of 1  $\mu$ g/L (Clausen et al. 2007b). Similarly, neither background well contained tungsten above 1  $\mu$ g/L. In contrast, tungsten was detected in MW-72S, located on the B Range floor, approximately 10 m downgradient of the impact berm. The first two samples, which were collected on December 15, 2005 and February 8, 2006, had tungsten concentrations of 15 and 25  $\mu$ g/L, respectively (Table 1).

Because of tungsten detections in December 2005 and February 2006, the Governor of Massachusetts ordered discontinuation of the firing of tungsten rounds in February of 2006. Removal of soil containing more than 150 mg/kg of tungsten took place between May 10, 2006 and June 21, 2006. A sample from MW-72S collected on May 10, 2006 showed an increase in tungsten concentration to 560 µg/L. At the time this water sample was collected, soil had not yet been removed from Bravo Range. The soil removal project spanned several weeks and consisted of removal of soil containing more than 150 mg/kg tungsten from the berms at B, C, and I Ranges (and other locations). A sample collected from MW-72S at the completion of the soil removal project (J2 documents open at same time June 21, 2006), showed tungsten had decreased to approximately 5 µg/L (Table 1). Ongoing sampling by the IAGWSP in 2007 and 2008 indicates concentrations have continued to decline and are presently less than 2 µg/L, suggesting surface soil removal activity was successful in mitigating tungsten release (Koenig 2008).

## 4.1.2 Phase II groundwater monitoring installations

Because results from Phase I showed tungsten had migrated to the aquifer in less than 6 years (based on data from well MW-72S on B Range; Clausen et al. 2007a, b), objectives for this Phase II investigation were to examine mechanisms by which tungsten migrated from surface soil to groundwater and to assess the extent of transport in the aquifer. To delineate the extent of tungsten migration at B, C, and SE/SW Ranges, eight drive points (temporary sampling points obtained with a Hydropunchtype sampler) and eight groundwater wells were installed in the fall of 2006.

Table 1. Summary of tungsten results for MW-72S (located on Bravo Range) and MW-123S (located downgradient between Bravo and Charlie Ranges).

All determinations used (ICP/MS).

		Tungsten Concentration (µg/L)				
Well	Sample	Lab - I	ERDC-EL	Lab - NAU		
Identification	Date	Filtered	Total	Total	Total (Dup)	
MW-72S	12/15/05	15	12	15	15	
MW-72S Dup	12/15/05	15	12	NS	NA	
MW-72S	2/8/06	22	NS	NS	25	
MW-72S	5/10/06	530	516/560	520	NS	
MW-72S	6/21/06	5	4	6	6	
MW-72S Dup	6/21/06	5	5	NS	NS	
MW-123S	6/21/06	< 1	< 1	< 1	< 1	
MW-123S	12/27/05	< 1	< 1	< 1	< 1	
MW-123S Dup	12/27/05	< 1	< 1	NA	NA	
MW-123S	2/8/06	< 2	NS	NS	< 1	
MW-123S	5/10/06	NS	< 1	< 1	NS	

Dup – duplicate; NA – not analyzed; NS – not sampled.

The drive points, lysimeters, and monitoring wells were installed in accordance with the draft Work Plan (Clausen et al. 2006). Drive-point and well locations on B Range were based on results from MW-72S and input from CENAE, IAGWSP, and regulatory agencies. Three drive points were installed at B Range and five at SE/SW Ranges (Table 2; Figures 1 and 2). Of the six originally planned monitoring wells, two were installed at B Range, one at C Range, and three at SE/SW Ranges. Because tungsten was not detected in any new drive points or monitoring wells, and drilling costs were lower than anticipated, two additional monitoring wells (one each at B and C Ranges) were installed in the third quarter of fiscal year 2007.

Table 2. Location and number of lysimeters, drive points, and monitoring wells installed in the Phase II Tungsten SAR Study.

Range	Deep Lysimeters	Drive Points	Monitoring Wells
Bravo	3	3	3
Charlie	0	0	2
SE/SW	0	5	3
Total	3	8	8

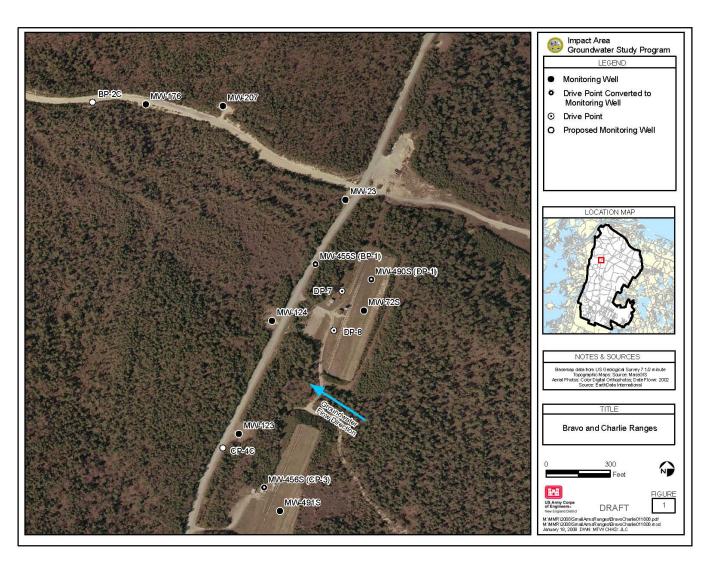


Figure 1. Location of drive points (DPs) and monitoring wells (MWs) at Bravo and Charlie Ranges.

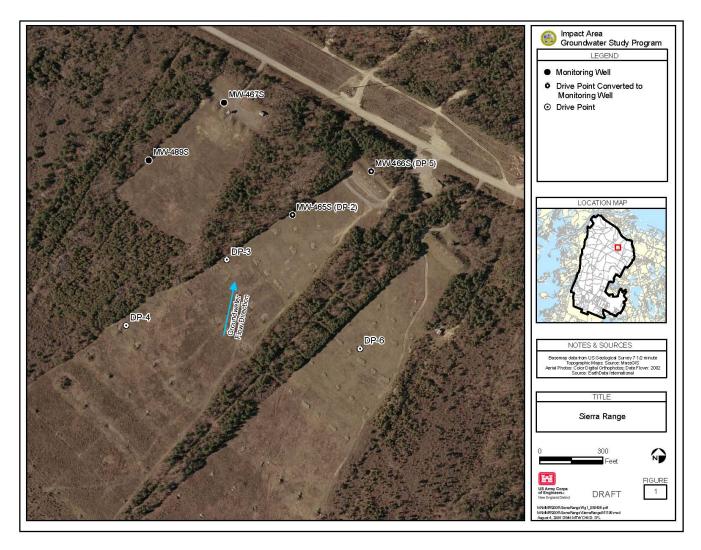


Figure 2. Location of drive points and monitoring wells at Southeast / Southwest Ranges.

#### 4.1.3 Background well evaluation

Part of the Phase II study included an extensive evaluation of the tungsten concentration in 12 background wells. The wells evaluated were selected by ECC, a subcontractor to the CENAE. Figure 3 shows their locations, and Table 3 provides construction details. ECC collected samples between April 3 and April 26, 2007 and submitted them to NAU for analysis. The tungsten concentrations in each of the 12 monitoring wells shown in Figure 3 were below the NAU detection limit of 0.5  $\mu$ g/L and below the reporting limit of 1  $\mu$ g/L (Table 4).

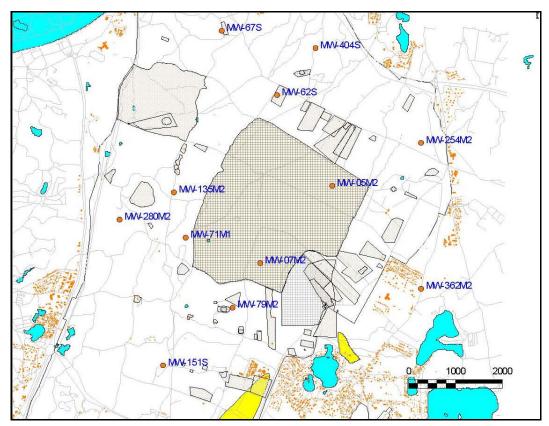


Figure 3. Location of sampled background wells.

Table 3. Well construction information for sampled background wells.

	Locatio	Surface Tota	Total	Total TOC	Screen Depth		Screen Elevation		
Well	UTM Coordinate	Elevation	Depth	Elevation	Тор	Bottom	Тор	Bottom	
Identification	Northing	Easting	(ft ngvd)	(ft bgs)	(ft ngvd)	(ft bgs)	(ft bgs)	(ft ngvd)	(ft ngvd)
MW-05M2	4619648.07	373613.26	184.21	215	183.83	170	175	14.21	9.21
MW-07M2	4617954.35	372065.76	176.80	247	176.74	170	175	6.80	1.80
MW-151S	4615732.98	369984.12	118.24	73	118.01	55	65	62.74	52.74
MW-182M1	4619561.37	369928.74	228.28	370	228.15	295	305	-66.72	-76.72
MW-254M2	4620589.00	375507.16	120.83	270	120.21	190	200	-69.17	-79.17
MW-280M2	4618918.50	369035.41	214.56	357	214.23	202	212	12.56	2.56
MW-357M1	4618397.33	375488.91	167.29	332	167.35	274	284	-107.22	-117.22
MW-404S	4622655.31	373252.47	231.60	240	231.62	181	191	49.94	39.94
MW-62S	4621618.51	372413.92	172.09	230	171.36	108	118	64.09	54.09
MW-67S	4623038.23	371234.69	200.11	307	199.61	161	171	39.11	29.11
MW-71M1	4618509.89	370464.21	226.01	315	225.35	180	190	46.01	36.01
MW-79M2	4616985.06	371469.62	159.09	191	158.45	116	126	43.09	33.09

ft ngvd – ft national geodetic vertical datum, ft bgs – ft below ground surface, TOC – top of casing.

Table 4. Tungsten concentrations in background groundwater monitoring wells.

Well ID	NAU Lab ID	Date Sampled	Preserved	Filtered	Tungsten Concentration (µg/L) (NAU)
MW-79M2	EC-S138801	4/26/2007	No	No	<1
MW-79M2	EC-S138802	4/26/2007	No	Yes	<1
MW-404S	EC-S138901	4/3/2007	No	No	<1
MW-404S	EC-S138902	4/3/2007	No	Yes	<1
MW-71M1	EC-S139001	4/26/2007	No	No	<1
MW-71M1	EC-S139002	4/26/2007	No	Yes	<1
MW-05M2	EC-S139101	4/25/2007	No	No	<1
MW-05M2	EC-S139102	4/25/2007	No	Yes	<1
MW-07M2	EC-S139201	4/25/2007	No	No	<1
MW-07M2	EC-S139202	4/25/2007	No	Yes	<1
MW-151S	EC-S139301	4/25/2007	No	No	<1
MW-151S	EC-S139302	4/25/2007	No	Yes	<1
MW-182M1	EC-S139401	4/26/2007	No	No	<1
MW-182M1	EC-S139402	4/26/2007	No	Yes	<1
MW-254M2	EC-S139501	4/24/2007	No	No	<1
MW-254M2	EC-S139502	4/24/2007	No	Yes	<1
MW-280M2	EC-S139601	4/26/2007	No	No	<1
MW-280M2	EC-S139602	4/26/2007	No	Yes	<1
MW-62S	EC-S139701	4/26/2007	No	No	<1
MW-62S	EC-S139702	4/26/2007	No	Yes	<1
MW-62S	NA	4/26/2007	Yes	No	<1
MW-62S	NA	4/26/2007	Yes	Yes	<1
MW-357M1	EC-S139801	4/25/2007	No	No	<1
MW-357M1	EC-S139802	4/25/2007	No	Yes	<1
MW-67S	EC-S139901	4/24/2007	No	No	<1
MW-67S	EC-S139902	4/24/2007	No	Yes	<1
MW-67S	NA	4/24/2007	No	No	<1
MW-67S	NA	4/24/2007	No	Yes	<1

NA = not applicable.

#### 4.1.4 Drive points

Eight temporary drive points (Table 2) were installed as part of Phase II of the tungsten study, with locations determined through consultation with CENAE, IAGWSP, and regulatory agencies. The drive-point drill rods were originally steam cleaned by the provider and also cleaned again just prior to drilling. An equipment blank sample collected from the drill rods showed no detectable tungsten. Drill rods were also cleaned between each drilling location.

Figure 1 shows locations of the three drive points installed on B Range. Drive-points DP-1 and DP-8, located on the northern and southern portion of the range, were placed in positions to assess whether tungsten was migrating into groundwater along the length of the berm face. DP-1 was located on the B Range floor between the berm face and the firing point, approximately half way between MW-72S and the northern end of the range. DP-8 was located behind the firing line approximately half way between MW-72S and the southern end of the range. DP-7 was located downgradient of MW-72S (west), approximately half way between MW-72S and well BP-1. The intent of DP-7 was to determine whether tungsten had migrated downgradient of MW-72S. Unfortunately, DP-7 yielded an insufficient quantity of water for performance of chemical analyses. This drive point may have become clogged with sediment or did not penetrate the water table sufficiently because of refusal.

Figure 2 shows five drive-point locations at the SE/SW Ranges. Four of these (DP-2, 3, 4, and 5) were drilled along the down-gradient (northwest) side of the range to determine whether tungsten was present in water and migrating away from the Ranges (Table 5). The water yield from both DP-3 and DP-4 was insufficient to analyze. DP-6 was installed on the SE Range down-gradient and 10 m (30 ft) from a pop-up target.

Depth-to-water was approximately 30 m (100 ft) for each drive point. The drill crew marked the rod in 1-ft increments as the drill approached the saturated zone. The crew were instructed not to exceed rig or rod capacities (i.e., stop before rod failure) unless they were very close to the saturated zone and the drive rod was still progressing downward (albeit slowly). Drilling was slowed near a depth of 30 m to ensure samples were collected at the water table. In some instances, rods and screens were left in place overnight in order to collect sufficient water. The drill rig apparently was unable to advance the drive point to a sufficient depth at several locations, and therefore no water could be collected.

Drive-point water samples were collected at 0-0.6, 0.76-2.29, and 2.29-3.81 m below the water table (bwt) (0-2, 2.5-7.5, and 7.5-12.5 ft bwt) using a Waterra sampler. Unfiltered and filtered water samples were sent to ERDC-EL for analysis of tungsten and other metals. Filtered water samples were sent to NAU for confirmation analyses. A split sample was provided to MADEP for analysis. Field parameters (temperature, pH, dissolved oxygen, specific conductance, turbidity, and Eh or redox potential) were measured and water samples were collected in 500-ml plastic bottles at each location.

Samples designated for filtering were filtered at ERDC-CRREL and sent to ERDC-EL for analysis. ERDC-EL analyzed the water for tungsten and metals using ICP-MS, following the USEPA Method 6020 for sample preparation by EPA Method 3005. Metals analysis included antimony, arsenic, chromium, copper, iron, lead, manganese, molybdenum, nickel, selenium, vanadium, and zinc (Appendix B).

Additionally, a sample was collected at the water table (0-0.6 m bwt [0-2.5 ft bwt]) from DP-5 for the IAGWSP for STL analysis of semi-volatile organic compounds (SVOCs) and explosives. All other water samples from the drive points were shipped to ERDC-CRREL.

All water samples from the drive points, with the possible exception of DP-2 located on the SW Range had no detectable tungsten (Table 5). Appendix B details the metal concentrations in the drive-point samples. ERDC-EL reported that tungsten concentration in the unfiltered water sample from DP-2 at the water table was 1.1  $\mu g/L$ . Neither NAU nor ERDC-EL reported tungsten in the filtered sample (Table 5; Appendix B). ERDC-EL reanalyzed the unfiltered sample and once again measured 1.1  $\mu g/L$  of tungsten. A split of this unfiltered sample was sent to NAU for analysis. NAU experienced interference issues and initially reported an estimated value of 91  $\mu g/L$ . Upon reanalysis, NAU reported the value as <15  $\mu g/L$ , because they were unable to achieve their expected reporting limit because of interference from suspended solids. NAU also filtered this sample, analyzed the filtrate, and did not detect tungsten.

In the second sampling interval at DP-2, NAU reported 4.3  $\mu$ g/L of tungsten in the filtered sample. In contrast, ERDC-EL reported no tungsten in either the filtered or unfiltered sample. NAU re-analyzed this sample, reported the amount of tungsten as < 3.0  $\mu$ g/L, and stated they could not

achieve a lower reporting limit because of sample matrix interferences. As discussed in the next section, a monitoring well was installed at this location. The well screen was located at the same depth as these possible drive-point detections. Tungsten was not detected in this monitoring well, suggesting drive-point detections (particularly the unfiltered samples) were false-positives caused by interference associated with suspended solids.

Table 5. Summary of tungsten results from drive points.

			Tungsten Concentration (µg/L)				
			Filtered		Unfiltered		
Range	Drive Point ID	Depth (ft bgs)	ERDC-EL	NAU	ERDC-EL	NAU	
	DP-1	112.1 - 114.6	<1	<15	<1	NA	
	DP-1 <sup>1</sup>	112.1 - 114.6	NA	<11	NA	NA	
	DP-1	114.6 - 119.6	<1	<15	<1	NA	
	DP-1 <sup>1</sup>	114.6 - 119.6	NA	<11	NA	NA	
	DP-1	119.6 - 124.6	<1	<15	<1	NA	
В	DP-1 <sup>1</sup>	119.6 - 124.6	NA	<11	NA	NA	
	DP-1	124.6 - 129.6	<1	<15	<1	NA	
	DP-1 <sup>1</sup>	124.6 - 129.6	NA	<11	NA	NA	
	DP-8	119.6 - 121.6	<1	<1	<1	NA	
	DP-8	122.1 - 127.1	<1	<1	<1	NA	
	DP-8	127.1 - 132.1	<1	<1	<1	NA	
	DP-2	138.1 - 140.1	<1	<11	1.1	91 J	
	DP-2 <sup>1</sup>	138.1 - 140.1	NA	NA	1.11	<15 <sup>1</sup>	
	DP-2	140.6 - 145.6	<1	4.3	<1	NA	
	DP-2 <sup>1</sup>	140.6 - 145.6	NA	<3.01	NA	NA	
SW	DP-2	145.6 - 150.6	<1	<15	<1	NA	
	DP-2 <sup>1</sup>	145.6 - 150.6	NA	<3.01	NA	NA	
	DP-5	136.3 - 138.8	<1	<1	<1	NA	
	DP-5	138.8 - 143.8	<1	<1	<1	NA	
	DP-5	143.8 - 148.8	<1	<1	<1	NA	
	DP-6	136.5 - 139	<1	<1	<1	NA	
SE	DP-6	139 - 144	<1	<1	<1	NA	
JE	DP-6	144 - 149	<1	<1	<1	NA	
	DP-6 <sup>2</sup>	144 - 149	<11	<11	<11	NA	

<sup>&</sup>lt;sup>1</sup>Laboratory duplicate; <sup>2</sup>Field duplicate; J – estimated concentration.

### 4.1.5. Monitoring wells

Locations of permanent groundwater monitoring wells were selected after researchers from USAEC, ERDC-CRREL, CENAE, IAGWSP, U.S. Geological Survey (USGS), USEPA, and MADEP reviewed all drive-point data. Three wells were then installed in B Range at drive-point locations BP-1 and BP-2C; two wells installed at C Range were at drive-point locations CP-3 and CP-2 (Fig. 1). Three wells were installed at the SE/SW Ranges (Figure 2). One well each was installed at drive-point locations DP-2 and DP-5; a third well was placed downgradient of the firing point at T Range, which is also downgradient of the SE/SW Ranges.

All wells were installed by a CENAE contractor who used a high-torque auger rig. The contractor (ECC) installed and developed the wells following the Impact Area Groundwater Study Program (IAGWSP) standard operating procedures specified in the Quality Assurance Project Plan. Drill holes were sufficient to allow installation of 5-cm (2-in.) diameter PVC pipe and 3-m (10-ft) long slotted screens. A single monitoring well was installed at each location. For each well installation, approximately 2 ft of the 10-ft screen were above the water table; the remaining 8 ft were submerged in the groundwater. Monitoring wells were equipped with dedicated bladder pumps compatible with controllers used by the IAGWSP contractors. A CENAE contractor developed the wells, and each was surveyed for elevation.

A MODFLOW 96 MMR-10NW Regional Groundwater Flow Model and MODPATH were used to simulate groundwater flow and predict the elevation of water at specific locations. The USEPA plume-diving calculator, available at web site: (http://www.epa.gov/athens/learn2model/part-two/onsite/diving.htm), was also used to determine whether well screens were placed at the correct depth to intercept groundwater originating from the ranges most likely to have tungsten. All samples were collected by the CENAE contractor and were sent to STL for analysis for IAGWSP. Some sample splits were collected and analyzed by ERDC-EL as part of this study. The majority of sampling events included collection of a filtered and unfiltered sample. Water samples from monitoring wells were less turbid than drive-point and lysimeter samples and allowed for lower detection limits. The tungsten detection limit for ERDC-EL was nominally 0.2  $\mu g/L$ , with a 1  $\mu g/L$  reporting limit.

Table 6 lists tungsten results for wells MW-455S and MW-490S installed at B Range for this Phase II study. Tungsten was not detected in either the filtered or unfiltered samples in the two sample splits provided to ERDC-EL. At C range, the Phase II-installed monitoring well MW-456S was sampled three times by STL for the IGAWSP. In the first sampling event, STL reported a tungsten detection of 2.6  $\mu$ g/L in the filtered sample and no tungsten in the unfiltered sample (Table 6). Unfortunately, split samples were not provided to ERDC for analysis. The two subsequent sampling events and analyses by STL for the IAGWSP indicated no tungsten was present. No tungsten was detected in the C Range Phase II well, MW-491S, by ERDC-EL in the split sample provided for this study.

At the SE/SW Range, split samples were provided to ERDC-EL from Phase II monitoring wells MW-465S and MW-466S. Neither well had detectable tungsten.

As reported by Clausen et al. (2007b), quality assurance/quality control data for ERDC-EL indicated no tungsten present in laboratory or field blanks. Thus, based on the seven water samples analyzed by ERDC-EL, no evidence of tungsten presence above the reporting limit was found in monitoring wells located immediately downgradient of the berms at B and C Ranges and the down-gradient edge of the range floor of the SW Range.

Detections of tungsten in MW-72S at B range were confirmed in filtered, unfiltered, acidified, and un-acidified samples by two independent laboratories using three different instruments/methodologies (Clausen et al. 2007b). Leaching of tungsten to groundwater from the B Range SAR was thus confirmed. However, samples collected prior to and after the highest reported value (560 µg/L in May 2006) suggest that tungsten elevation occurred during a limited time period. Oscillating concentrations of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and perchlorate have been observed in monitoring wells downgradient of Demolition Area 1 at MMR and appear related to overall precipitation trends. The MW-72S anomalous value was possibly related to similar phenomena. Unfortunately, data are insufficient to determine whether the period of elevated tungsten lasted hours, days, weeks, or months. However, the zone of elevated tungsten is apparently limited and will migrate to the northwest away from the B Range. Although dispersion within the aquifer is low, the zone of contamination will disperse, and the foot print of elevated tungsten will grow with time. Concomitant with an increase in the area of elevated contamination, tungsten concentration will decline with time because of dispersion and subsequent dilution.

Table 6. Monitoring well results for Tungsten Study Phase II wells.

					Tungsten Concentration (µg/	
Well ID	Drive Point ID	Range	Sample Date	Filtered/ Unfiltered	Phase II Study Results ERDC-EL	IAGWSP Results STL
MW-455S	BP-1	В	9/26/06	F	< 1	
MW-455S	BP-1	В	9/26/06	U	< 1	
MW-490S	NA	В	5/14/07	F	< 1	
MW-490S	NA	В	5/14/07	U	< 1	
MW-490S	NA	В	5/14/07	U, LD	< 1	
MW-456S	CP-3	С	11/6/06	F	NS	2.6
MW-456S	CP-3	С	11/6/06	U	NS	< 1
MW-456S	CP-3	С	3/28/07	F	NS	< 1/< 1
MW-456S	CP-3	С	3/28/07	U	NS	< 1/< 1
MW-456S	CP-3	С	7/31/07	U	NS	< 1
MW-456S	CP-3	С	7/31/07	U, FD	NS	< 1
MW-491S	NA	С	5/14/07	F	< 1	
MW-491S	NA	С	5/14/07	U	< 1	
MW-465S	DP-2	SE/SW	10/13/06	F	< 1	
MW-465S	DP-2	SE/SW	10/13/06	U	< 1	
MW-465S	DP-2	SE/SW	10/25/06	F	< 1	
MW-465S	DP-2	SE/SW	10/25/06	U	< 1	
MW-466S	DP-5	SE/SW	10/13/06	F	< 1	
MW-466S	DP-5	SE/SW	10/13/06	U	< 1	
MW-466S	DP-5	SE/SW	10/13/06	F, FD	< 1	
MW-466S	DP-5	SE/SW	10/13/06	U, FD	< 1	
MW-466S	DP-5	SE/SW	10/25/06	F	< 1	
MW-466S	DP-5	SE/SW	10/25/06	U	< 1	

NA = not applicable, NS = no sample, J = estimated value, F or U = filtered/unfiltered.

Because tungsten projectiles were used for a short period of time (< 6 years), the maximum extent of contamination in groundwater downgradient of MW-72S can be estimated. Groundwater flow velocity is approximately  $0.3 \, \text{m/day}$  (1 ft/day) (AMEC 2001a), yielding a maximum horizontal distance of 2,190 ft [for the 6 years of tungsten presence], which conservatively assumes very rapid transport through the vadose zone. The flow rate through the unsaturated zone has not been measured, but model-

FD = field duplicate, LD = laboratory duplicate.

<sup>&</sup>lt;sup>1</sup>STL results with multiple values indicate acidified and un-acidified samples.

ing activities and discussions with USGS personal suggest that a conservative tracer would take several weeks to several months to move from the ground surface to the top of the water table. The lack of tungsten detections in the drive points and down-gradient wells at B Range confirm that any zone of elevated tungsten contamination is limited in size.

In addition to sampling monitoring wells installed as part of the Tungsten Phase II SAR Study, the CENAE/IAGWSP contracted directly with NAU and ERDC-EL to provide analysis on split samples for several IAGWSP wells. CENAE also conducted an extensive, blind, round-robin test between ERDC-EL, NAU, STL, and MADEP laboratories. These data (not reported here but available from the CENAE/IAGWSP) showed sufficient agreement among laboratories. Thus, analytical problems may be discounted when reviewing tungsten data.

#### 4.2 Task 3 – Unsaturated zone evaluation

### 4.2.1 Historical perspective – summarized Phase I lysimeter results

Table 7 summarizes the lysimeter results for Phase 1 of the Tungsten SAR study (Clausen et al. 2007b). Concentrations as high as 400 mg/L were observed in lysimeters installed beneath the berm face. As reported previously, data from these shallow lysimeters were not consistent with respect to concentrations trends; some increased, others decreased, and still others showed no trend. Background concentrations of tungsten were generally reported as less than 0.2 mg/L.

#### 4.2.2 Phase II shallow lysimeters

The Phase II shallow lysimeter task involved sampling the lysimeters remaining from Phase I. Several lysimeters were no longer available for Phase II sampling. When berm soils containing > 150 mg/kg tungsten were removed by the MAARNG, several of the lysimeters, including all of those at B Range, were damaged during soil removal. In addition, several lysimeters, including those at background locations, were damaged by winter freezing. Three undamaged lysimeters (MMR-18, 19, 20, and 21) were available for sampling at C Range, and two (MMR-9 and 12) were available at I Range.

B-range Phase 1 data are presented in Figure 4. The data indicate a decline in tungsten concentration with time.

Table 7. Shallow lysimeter Phase I tungsten results (mg/L).

Lysimeter ID	Range	Location	Depth (cm bgs)	10/20/05	11/9/05	12/15/05	05/10/06	Mean
1	В	TR	78	85	48	55	28	54
2	В	TR	84	18	No water	24	15	19
3	В	TR	61	22	27	4	18	28
5	В	BP	69	60	102	No water	23	62
6	В	BP	107	312	253	No water	53	206
7	В	BP	91	No water	164	137	38	113
8	В	BP	112	314	290	256	No water	287
Bravo Range Me	ean			135	148	103	29	110
9	I	TR	41	11	6.0	6.8	No water	7.8
10	I	TR	25	0.06	0.07	< 0.05	0.02	0.05
11	1	TR	71	0.09	< 0.05	< 0.05	0.02	0.06
12	1	BP	109	0.15	0.21	0.43	0.39	0.29
14	I	BP	36	0.24	0.27	0.24	0.60	0.33
India Range Me	an			2.3	1.6	2.5	0.26	1.7
17	С	TR	46	1.3	1.9	No water	3.0	2.1
18	С	TR	117	5.5	6.4	7.7	8.1	6.9
19	С	TR	109	5.4	8.3	11	8.5	8.2
20	С	TR	46	5.3	6.6	14	25	12
21	С	BP	165	260	400	No water	262	308
22	С	BP	119	116	206	96	44	115
24	С	BP	58	32	53	72	52	52
25	С	BP	163	139	79	110	261	147
26	С	BP	135	337	145	105	35	155
Charlie Range Mean			100	101	59	78	90	
15	1	Bckd	53	No water	< 0.05	No water	0.01	
27	С	Bckd	46	NI	NI	NI	0.17	
28	В	Bckd	46	NI	NI	NI	No water	
Overall Mean				86	95	63	42	

TR - trough; BP - bullet pocket; Bckd - background; NI - not installed.

At C Range, shallow lysimeters showed a weak tungsten-concentration decreasing trend prior to the cessation of training with tungsten projectiles (Figure 5). Tungsten concentrations remained low after the cessation of training and the soil removal project (April and June 2006). The lysimeters remaining after soil removal continued the declining tungsten-concentration trend.

Initial tungsten concentrations measured at I Range lysimeters were much lower than those for B or C Range because I Range had an order of magnitude fewer tungsten projectiles fired than the other two ranges (Figure 6).

The lowest tungsten level for lysimeter 9 occurred after the cessation of tungsten firing and soil removal, but the decrease was modest. Lysimeter MMR-12 was at a low level prior to and after cessation of training with tungsten projectiles.

Overall, shallow lysimeter results indicate that tungsten concentrations in the pore water decline after cessation of training and after the removal of soil. However, some tungsten remains in the pore water because of previous or continuing dissolution and transport through the shallow soil profile.

All shallow lysimeters sampled during Phase II remain in place and are presumably available for additional sampling. Although Figures 4 through 6 show precipitation amounts, there is no evidence of a trend for tungsten concentration that is attributable to precipitation. Whether this is a consequence of inadequate sampling frequency or lack of a relationship with precipitation is unknown. However, later laboratory experiments suggest a probable relationship between intensity and duration of rainfall and tungsten concentrations.

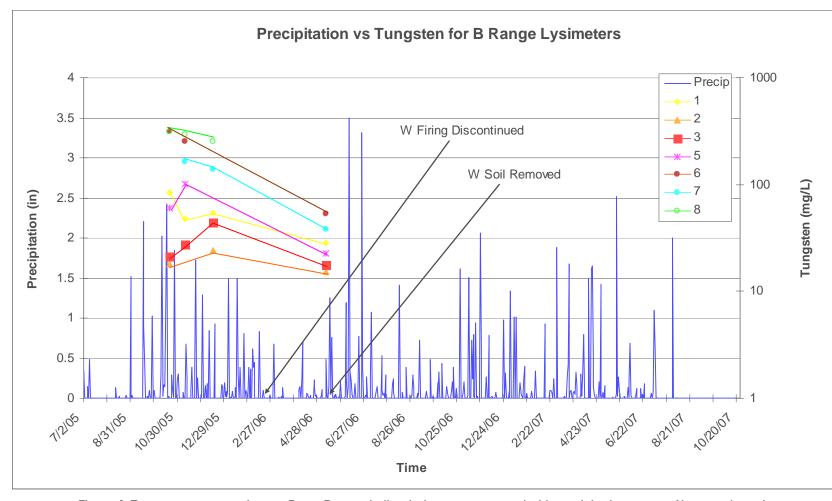


Figure 4. Tungsten concentrations at Bravo Range shallow lysimeters compared with precipitation events. Also noted are times when the use of tungsten (W) bullets ceased, and soil removal occurred.

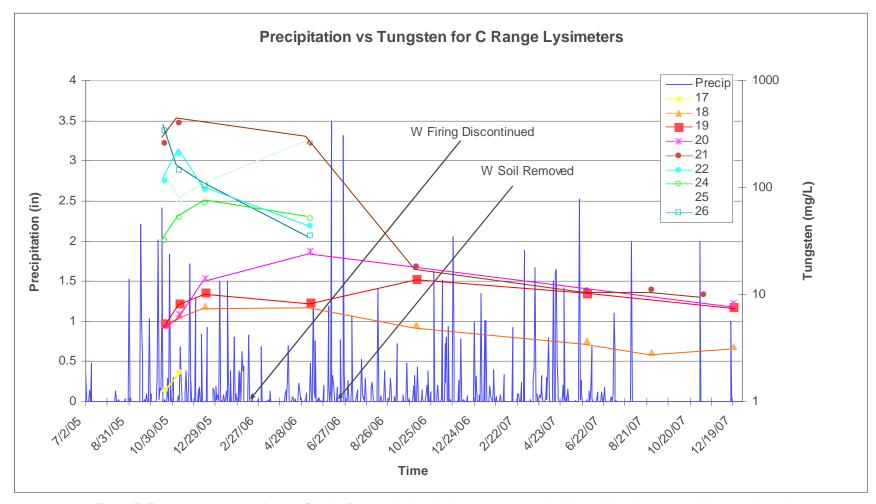


Figure 5. Tungsten concentrations at Charlie Range shallow lysimeters compared with precipitation events. Also noted are times when the use of tungsten (W) bullets ceased and soil removal occurred.

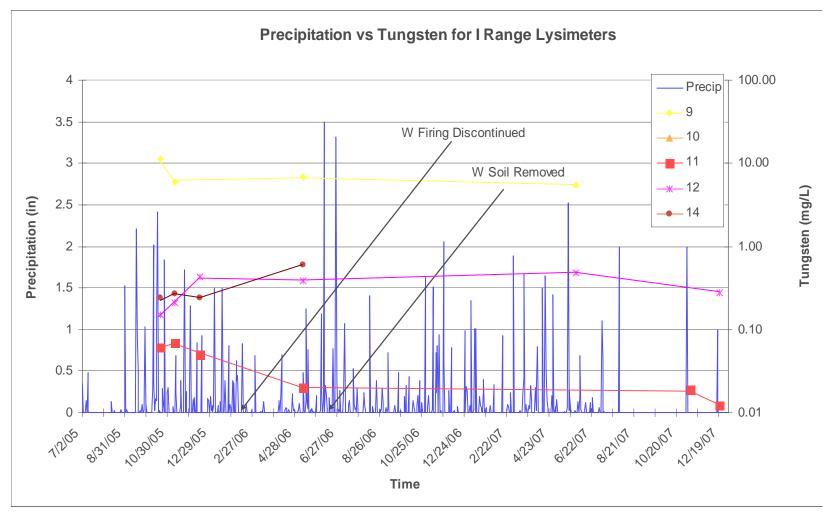


Figure 6. Tungsten concentrations at India Range shallow lysimeters compared with precipitation events. Also noted are times when the use of tungsten (W) bullets ceased and soil removal occurred.

#### 4.2.3 Phase II deep lysimeters

Three deep lysimeters were installed beneath the former lower berm at B Range for the Phase II study. The purpose of these lysimeters was to assess unsaturated zone transport deeper in the soil profile than that observed with shallow lysimeters. This location had the highest tungsten concentration in surface soil prior to the removal project and was near MW-72S, which was the groundwater well with tungsten contamination. Depths for lysimeters were arbitrarily selected but were kept shallower than 10 m to allow sampling with a peristaltic pump. Lysimeter installation by the CENAE contractor was conducted with the same high-torque auger drilling rig used for installation of the monitoring wells. Holes were drilled to depths of 1.5, 4.6, and 7.2 m [5 ft (Lysimeter #30), 15 ft (Lysimeter #31), and 25 ft (Lysimeter #32)]. Lysimeters were sampled by ERDC-CRREL personnel using methods described in Clausen et al. (2007b). Analyses were performed by ERDC-EL.

These lysimeters have been sampled on six occasions (Table 8). Tungsten concentrations are highest in the shallowest (5 ft) lysimeter (#30). Tungsten was detected in the middle (#31, 15 ft) lysimeter, but concentrations were consistently less than 5  $\mu$ g/L. Results for the deepest lysimeter, (#32, 25 ft), show a declining trend for the three samples recovered. Complete metal and field parameter results for these samples are provided in Appendix C.

Figure 7 shows the Camp Edwards precipitation record with superimposed tungsten concentrations from deep lysimeters and MW-72S at B Range. No cause-and-effect relationship is evident between precipitation and groundwater tungsten concentrations even when accounting for lag time between a precipitation event and a measured tungsten concentration. These data demonstrate that the concentration of tungsten in the soil pore-water declines with depth. The decline is a probable consequence of dilution, but some tungsten may be changing to a less-mobile form due to speciation and is adsorbing to soil (Bednar et al. 2008).

Table 6. Taligater Friday taligater results (pg 2) for deep lysimeters at brave hange.							
		Tungsten Concentration (µg/L)					
Lysimeter ID	Depth (ft)	11/3/06	2/28/07	5/3/07	8/27/07	11/08/07	12/19/07
30	5	660	NW	1,436	NW	NW	1,432
31	15	NW	< 2	4.1	NW	< 5	< 5
32	25	108	37	13	NW	NW	NW

Table 8. Tungsten Phase II Study tungsten results (ug/L) for deep lysimeters at Brayo Range.

NW - no water.

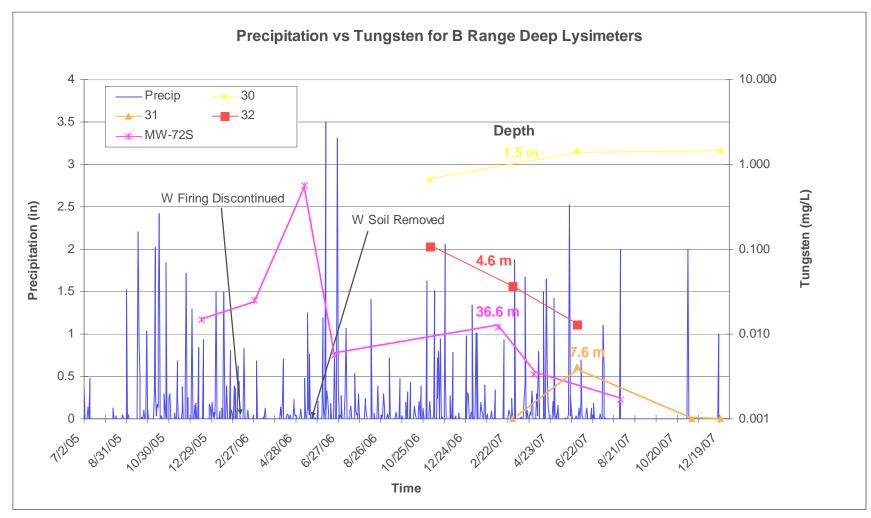


Figure 7. Tungsten concentrations from deep lysimeters and MW-72S at B Range compared with precipitation events at Camp Edwards. (Note the "X" m value represents the depth of the associated sampling device).

#### 4.3 Task 4 – Dissolution studies

A month-long laboratory drip test and a year-long outdoor test with two bullet fragments were conducted to examine the rate at which tungsten dissolved from bullet fragments. A third batch test that involved both dissolution and desorption was conducted and is included in this section because the dissolution mechanism was likely predominant.

#### 4.3.1 Laboratory drip test

In the 30-day laboratory drip test, DI was dripped onto a 102.98-mg tungsten nylon bullet fragment (Figure 8a), using a syringe pump (Fig. 8b). The drip rate, 0.51 mL/hr (~ 30- $\mu$ L drops at a rate of 20 drops/hr), was equivalent to rain falling at 5.5 mm/hr (~0.2 in. /hr), resulting in an accumulation of approximately12 mL of water each day. Water flowed across the fragment and through a supporting glass frit into a clean scintillation vial. Analyses of the daily samples showed tungsten from the fragment was readily soluble (Figure 9). Concentrations of the daily dissolution varied between 4 and 13 mg/L, with an average of 7.2  $\pm$  2.3 mg/L. An adequate mass balance for the experiment was demonstrated by weighing the bullet fragment at the end of the test. The fragment lost approximately 2 mg (102.98- 101.1 mg) of weight. Using the average volume of water, 11.2 mL, and assuming no error in the ICP-MS measurements, ~ 2.4 mg of tungsten was recovered in the water samples.

#### 4.3.2 Outdoor exposure test

Two tungsten/nylon cores (Figure 10a) were set up outdoors in 4-cm diameter Buchner funnels on top of liter bottles (Figure 10b). The two tungsten/nylon cores, labeled W1 (dark in color) and W2 (silver in color), weighed 2.06 and 2.07 g, respectively. Rainwater or snowmelt that fell naturally onto the tungsten cores was collected in the bottles. Approximately every 2 weeks, the bottles were changed and the accumulated water volume was measured. Aliquots of the samples were then submitted for analysis. The results are shown in Figure 11. The W1 test was stopped in November 2007, and the W2 test is still ongoing. No water samples were collected over the winter (December 2007 through April 2008) when the experiment was covered with snow. The dark W1 core released tungsten immediately, and several months passed before leaching was observed from the silver W2. An assumption was made that darker W1 material was already oxidized to some extent and, therefore, was more readily dissolved. The silver color of the longer-reacting W2 fragment indicates pure tungsten metal. Thus, there was a time lag until sufficient surface oxida-

tion occurred for the fragment to begin to dissolve. In both cases, loss of tungsten from both the W1 and W2 cores approached 2 to 2.5 mg over a 3-month period, which was equivalent to a loss of approximately 0.022 to 0.028 mg tungsten per day. In the indoor test, the tungsten loss after 30 days was approximately 2 mg or 0.067 mg/day. The higher rate of tungsten loss from the indoor experiment is a function of a more constant and greater rate of water contact with the tungsten particulate and related surface area. Intact tungsten cores were used in the outdoor experiment, whereas in the indoor experiment a tungsten fragment from a core was utilized. Additionally, in the outdoor experiment, the precipitation contact was more irregular, which may have resulted in formation of tungsten oxides that dissolved more slowly.

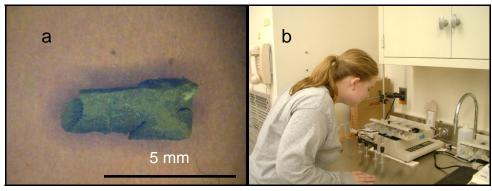


Figure 8. (a) Tungsten/nylon core fragment used in the laboratory dissolution test and (b) the laboratory apparatus.

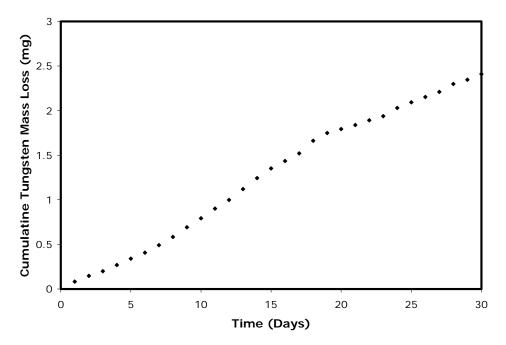


Figure 9. Tungsten mass dissolved (mg) in water samples taken over 30 days.

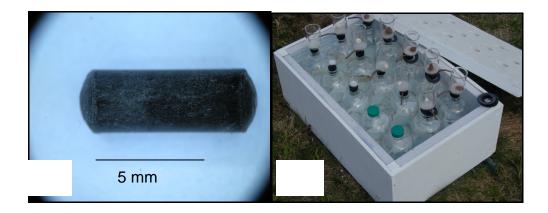


Figure 10. Photograph of a tungsten-nylon core (a) and outdoor experimental apparatus (b).

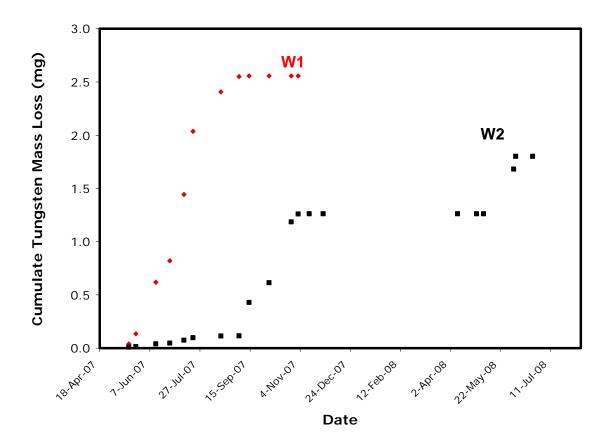


Figure 11. Cumulative mass loss of tungsten (W) in water samples collected from the bullet cores placed outdoors.

If one assumes that the outdoor loss rate of 2 mg every 30 days is representative, knows an intact tungsten/nylon core contains 2,010 mg tungsten, and is aware of soil concentration, a rough estimate of the persistence of tungsten as a particulate in soil can be determined. If a tungsten soil concentration of 2,000 mg/kg is assumed, this would be equivalent to

a single tungsten/nylon core. The persistence of the tungsten core is then approximately 83 years. However, we suspect that the rate of tungsten dissolution is dependent on surface area. An intact tungsten core has a much lower surface area than individual particles. The predominant form of tungsten present in the soil is believed to be comprised of tungsten particles ranging from 5 to 20 microns in size. However, the tungsten rate loss for varying size particles is unknown, suggesting that an 83-year value of tungsten persistence is conservative.

#### 4.3.3 Batch test of contaminated soil

Seventeen soil samples contaminated with tungsten were collected from the SAR and tested. These soils might contain both metallic tungsten and tungsten sorbed to the soil surface, with the proportional distribution of each unknown. Consequently, this experiment is not strictly a dissolution or desorption test but rather a combination of the two processes. One assumed is that the mechanism for tungsten deposition and the rate of weathering in the field is the same for all samples. Therefore, a second assumption is that distribution of tungsten metal and tungsten sorbed onto the soil is essentially the same for each sample.

To begin the test, 4.5~g of soil that was previously sieved to remove the > 2~mm fraction was added to a 4-oz amber glass container. Seventy ml of deionized water (DI) was added to the 4.5~g soil. The samples were allowed to equilibrate for 24~hr on an orbital shaker table mixing at 100~r evolutions per minute (rpm). After 24~hr the test samples were allowed to settle for 2~hr, and the aqueous solution was pipetted off and placed into a 100~r ml plastic container and chilled prior to analysis.

Results from this test show that the amount of tungsten in solution is a function of soil concentration, and tungsten loss occurs in a typical concentration gradient pattern. A greater percentage of loss is observed in soil samples with higher tungsten soil concentrations, and a lower rate of loss (91 to 15%) occurs in soil with lower tungsten soil concentrations (Table 9). These results suggest initially that the rate of tungsten loss via either dissolution or desorption is high, but as concentration in the soil declines, the rate of loss also declines. Previous calculations of tungsten loss from a hypothetical, initial 2,000 mg/kg tungsten-contaminated soil in Section 4.3.2 may be an underestimation. Additionally, results from this experiment indicate that tungsten is rapidly dissolved or desorbed from soil.

Table 9. Dissolution/desorption batch test results.

Sample ID	Soil Concentration (mg/kg)	Measured Leachate Concentration (mg/L)	Mass Loss of Tungsten in 24 hr (mg)	Mass Loss of Tungsten in 24 hr (%)
MMRBMB022S1	1534	70.6	4.9	72
MMRBMB030S1	1508	60.3	4.2	62
MMRBMB032S3	1430	68.9	4.8	75
MMRBMB023S2	1422	77.2	5.4	84
MMRBMB031S2	1371	60.6	4.2	69
MMRBMB036S3	1079	62.8	4.4	91
MMRCBMB007S3	1505	82.9	5.8	86
MMRCMB009S2	733	22.9	1.6	49
MMRCMB011S3	672	23.2	1.6	54
MMRCTR006S2	339.	5.86	0.4	27
MMRCTR010S3	317	7.03	0.5	34
MMRCTR003S1	290	3.83	0.3	21
MMRILB003S3	369	11.8	0.8	50
MMRITR013S3	212	2.66	0.2	20
MMRITR009S2	209	3.23	0.2	24
MMRITR002S1	193	3.65	0.3	29
MMRIBB004S1	113	1.06	0.1	15

#### 4.3.4 Dissolution experiment summary

The amount of tungsten dissolving in each water droplet likely depends on the contact time between tungsten, water, and the amount of water passing by the tungsten particle. For the laboratory test, the tungsten fragment represented a large reservoir. Consequently, the water dripped on it depleted a small consistent portion of the available tungsten resulting in a constant loss rate. Tests conducted outdoors are more difficult to interpret because periods of tungsten dissolution are followed by periods of no apparent tungsten release. The latter observations are probably a consequence of varying temperature, humidity, air contact, and development of oxide coatings. Nonetheless, the study demonstrates how easily some tungsten particles dissolve under ambient conditions. Dissolution/desorption batch experiments with contaminated soil show the rate of tungsten loss is further complicated when tungsten metal is introduced

to the soil. However, the rate of tungsten dissolution/desorption in soil is rapid. Given additional variables of interaction of tungsten with soil and the short duration of these experiments, extrapolation of tungsten particle persistence in soil is not possible.

### 4.4 Task 5 - Sorption and desorption laboratory studies

The purpose of sorption/desorption experiments was to measure the equilibrium distribution coefficient  $(K_d)$  for tungsten in order to predict the amount of tungsten that adsorbed to the soil matrix.  $K_d$  is used in computer models to assess the transport of tungsten through the soil matrix.

Desorption experiments are used to assess whether sorption is a linear and reversible reaction. If sorption is reversible, derived distribution coefficients from the sorption tests can be used to predict how rapidly tungsten desorbs from the soil over time. Instead of starting with clean soil and contaminated water, sorption experiments use clean soil and contaminated water, and desorption experiments use clean water and contaminated soil, as tungsten moves from the soil to the water during the incubation period. As with sorption experiments, if appropriate concentration measurements and mass balances are performed, a  $K_d$  value can be estimated from the data. If sorption is reversible,  $K_d$  values determined in the sorption and desorption experiments are identical. If sorption is not completely reversible, the desorption  $K_d$  value will be larger than the sorption value. The difference between the two values provides the degree of irreversible sorption (or very slow desorption).

#### 4.4.1 Batch experiments

In general, the batch experiments were conducted following American Society of Testing Methods (ASTM) Method D4646 (ASTM 2008). However, the first set of experiments focused on assessing the change in  $K_d$  over time, and thus experiments were not limited to a 24-hr interval as specified in the ASTM methodology.

#### 4.4.1.1 Effect of time on sorption partitioning coefficients

In a previous study, sorptive  $K_d$  for tungsten was measured on 18 soils (sodium tungstate initial-spiking solution) over several time intervals to 120 days (Larson 2008, personal communication). For 12 of the 18 soils, significant (up to  $\sim 700$  times larger) increases in the sorptive  $K_d$  were noted

with time (to 120 days). These large  $K_d$  changes over time could be a consequence of physical factors, such as diffusion in the tortuous media or intercalation within smectitic clays. Changes in soil and soil solution geochemical parameters because of redox reactions are the more likely cause of  $K_d$  changes over time. According to Bednar et al. (2008), dissolved tungsten changes its speciation with time, forming less mobile species, and soil redox potential is decreased as tungsten dissolves. Linked to the latter phenomena are the redox status and pH of soils and their effect on both the speciation of tungsten and hydrous oxides of iron and manganese. Previous work using a variety of soil types and contaminants demonstrated a significant role of hydrous oxides for assessing migration of oxyanions similar to tungsten, such as arsenic, selenium, chromium, and vanadium (Jenne 1968; Korte et al. 1976).

The results presented below describe measurements of  $K_d$  for soils from Camp Edwards and address whether  $K_d$  changes as a function of time. Each experiment was performed in triplicate using DI spiked with sodium tungstate. The aqueous tungsten concentrations were fitted to the linear Freundlich isotherm model for calculation of partition coefficients using four different concentrations (0.1, 1,100, and 1,000 mg/kg).

Table 10. Grain size distribution of Camp Edwards soils used for partition coefficient determinations.

Sample ID	% Sand	% Silt	% Clay	Soil Classification
Soil 1 MMR-A1	77	7	16	Sandy Loam
Soil 2 MMR-A2	85	4	11	Sandy Loam
Soil 3 MMR-J1	93	1	6	Sand
Soil 4 MMR-J2	89	6	5	Sand
Soil 5 MMR-T1	58	19	23	Sandy Clay Loam
Soil 6 MMR-T2	74	8	18	Sandy Loam

Six soils, including three sandy loams, two sands, and one sandy clay loam were used for the tungstate sorption  $K_d$  determinations (Table 10). The soils contained no tungsten from SAR firing, nor were they treated with Maectite — a proprietary phosphate-based agent used to stabilize lead in the SAR berm soils at Camp Edwards. The samples were collected in presumed background locations at the A, J, and T Ranges. Each sample consisted of a 50-increment surface sample collected from 0 to 2.5 cm over a random area. A presumption was that this approach would yield a soil sample largely representative of the entire range.

Twelve g of air-dried homogenized soil were weighed and placed into 125-mL high-density polyethylene bottles. Each bottle was filled with 120 mL of DI containing dissolved tungsten (as sodium tungstate), nominally at 0, 10, 20, 50, and 100 mg/L; and each concentration was spiked in triplicate for a total of 15 bottles. The zero-spike level was used to determine if any natural tungsten was present in the soil; since no tungsten was detected in the zero spike level samples, these were indeed background samples.

The bottles were agitated on a reciprocating shaker throughout the experiment. Half-ml aliquots were collected and filtered at 1-, 30-, 60-, 90-, 120-, and 180-day intervals for  $K_d$  determinations. All samples were analyzed on a Perkin Elmer Elan DRC II ICP-MS. The aliquots were diluted as appropriate for ICP-MS analysis (20 to 1,000 times dilution factors), according to standard methods developed at ERDC-EL, and using Terbium-159 and Holmium-165 as internal standards. Second- and third-source tungsten check standards were also analyzed with each analytical batch to verify instrumental accuracy. Sample analysis followed the procedures outlined in Clausen et al. (2007b).

Concentration data (Table 11; Appendix D) were plotted on a logarithmic scale to determine  $K_d$  by using the linear Freundlich isotherm model (Langmuir 1997) in which  $K_d$  values are calculated as the antilog of the intercept of the linear regression line. Use of the linear model was supported for this study because the correlation coefficients ( $r^2$ ) for most soils and time intervals were greater than 0.90. Two of the soils, however, have limited sorption capacity for tungsten and had correlation coefficients of 0.7 or less, suggesting the highest spike value was large enough to result in non-linear sorption.

At completion of the 180-day experiment, a final aliquot was collected from the 10 mg/L spike samples and analyzed by HPLC-ICP-MS for tungsten speciation, following a modification of the method of Bednar et al. (2007). An Agilent 1100-HPLC equipped with a Shodex KW-803 size exclusion column was interfaced to the Perkin Elmer Elan DRC II to determine tungsten speciation by size. This analysis indicated that some polytungstates formed in the sorption experiment solutions during the 180-day experiments.

Previous work by Bednar et al. (2008) suggests that these speciation changes will affect sorption of tungsten to soils, and polytungstates will have a larger  $K_{\rm d}$ .

A plot of tungsten  $K_d$  versus time for these six soils indicates an increase from 30 to 60 days for four of the soils and a stabilization of  $K_d$  thereafter (Fig. 12). The other two soil  $K_d$  values continued to increase until 120 days; measured values remained similar or decreased slightly thereafter.

These results can be compared with those obtained by Larson (personal communication, 2007) on soils classified as sandy silt from Camp Edwards. Larson reported a maximum result of  $\sim 90$  mL/g after approximately 40 to 50 days. Larson's data compare well to the time required to achieve a steady state in this study, although the  $K_d$  results for coarser soil in this study were approximately three times greater. Larson used soil with a pH of 4.9. Using a silty loam soil, Bednar et al. (2008) reported a  $K_d$  of 141 mL/g at pH 7, which is in the same range reported in this study.

Table 11. Tungsten sorption soil partition coefficients in batch studies at six elapsed times.

	Sorption Partition Coefficient K <sub>d</sub> (L/kg) *					
Time	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6
(days)	MMR-A1	MMR-A2	MMR-J1	MMR-J2	MMR-T1	MMR-T2
	18	33	117	2	89	210
1	19	42	120	2	89	199
	16	39	123	2	90	205
	25	36	101	25	80	183
15	24	38	102	25	79	172
	25	40	104	25	80	182
	120	143	273	111	250	334
30	116	148	273	104	259	315
	120	149	263	109	256	341
	115	120	211	116	323	300
60	128	146	214	108	338	293
	119	148	224	119	356	282
	107	115	214	135	329	313
90	108	147	230	117	318	297
	104	135	212	134	359	305
	92	150	257	114	445	397
120	97	165	257	114	459	378
	93	169	249	102	466	401
	77	154	232	139	336	371
180	91	171	237	125	350	327
	110	168	241	134	337	361

<sup>\*</sup>Raw data are presented in Appendix D.

Results suggest the standard 24-hr batch sorption test protocol, as defined by ASTM, is inappropriate for determining tungsten  $K_ds$ . Use of the ASTM method will result in under prediction of the degree of tungsten sorption and ultimately will over predict the rate of movement.

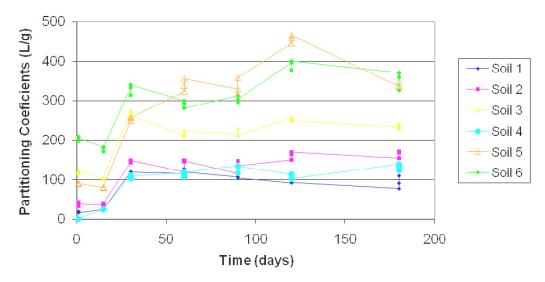


Figure 12. Tungsten sorption partition coefficients from soil batch tests.

#### 4.4.1.2 Effect of different substrates on tungsten sorption/desorption

Brief laboratory batch experiments were performed to examine the relative ability of several materials to sorb and desorb tungsten. Experimental conditions were not controlled with respect to pH and redox potential, and the experimental time frame was brief, i.e. 24 hr. Hence, the results can only be considered preliminary.

In the experiment sorption phase, 4.5 g of material was added to a 4-oz amber glass container. This material was spiked with a 70-ml solution containing 10 mg/L sodium tungstate. Samples were equilibrated for 24 hr on an orbital shaker table at 100 rpm. After 24 hr the test samples were allowed to settle for 2 hr, and the aqueous solution pipetted off, placed into a 100-ml plastic container and chilled prior to analysis. After the leachate was removed, the material was allowed to air dry.

The same soil used in the sorption phase of the test was spiked with 70 ml of DI, which was added to 4.5 g of soil. Samples were equilibrated for 24 hrs on an orbital shaker table at 100 rpm. After 24 hr, test samples were allowed to settle for 2 hr; the aqueous solution was pipetted off, placed into a 100-ml plastic container, and chilled prior to analysis.

Three pure materials were tested: aluminum oxide (Linde "A" polish, a pure grade), goethite, and kaolinite. Specific attributes of these materials were not measured except for their efficiency in sorbing tungsten. For kaolinite, individual sources can yield significant variation in physical properties. Nonetheless, aluminum oxide was expected to be the better sorbent because this material has a zero point charge close to a pH of 8 (Schulthess and Sparks 1987). Because the surface charge on aluminum oxide (and goethite) becomes more positive with increasing acidity, the lower the pH, the more easily the tungstate anion is retained. Based solely on charge considerations, goethite, with a zero point of charge near neutral and a less steep increase in positive charge with increasing acidity (Langmuir 1997), should be less effective than aluminum oxide. Although recent work (Schroth and Sposito 1997) has reported a zero point charge between pH 5 and 6 for kaolinite, the literature includes many pH values in the range of 3 to 4. Consequently, this single-layer clay may have a significant negative charge at low pH (Langmuir 1997) and may not be an effective sorbent for tungstate under acidic conditions.

These pure materials were compared to three soils: Ottawa Sand, a forest soil from Camp Edwards (selected because visual inspection indicated a greater than typical organic matter content for site soils), and a sample designated as MMRBMB022S1. The latter soil was a contaminated SAR soil containing 1,530 mg/kg of tungsten obtained from the middle berm area on Bravo Range. Because the MMRBMB022S1 sample was obtained from the SAR, it is presumed to contain both metallic tungsten and tungsten sorbed to the soil surface. Although MMRBMB022S1 soil was spiked with sodium tungstate, the presence of anthropogenic metallic tungsten suggested the desorption test also includes a dissolution component; this is unlike the other materials tested that have only a desorption component Therefore, the results for the MMRBMB022S1 sample represent both desorption and dissolution processes.

As expected, aluminum oxide was the most sorptive material and was two orders of magnitude more efficient than Camp Edwards forest soil, which is the second highest sorptive material (Appendix E). Pure Ottawa Sand was approximately half as effective as soil from the forest area. MMRBMB022S1 was almost as effective as Ottawa Sand, although any evaluation of MMRBMB022S1 must be tempered with awareness that this soil was already highly contaminated with metallic tungsten from firing activities, with a portion of the tungsten previously dissolved and sorbed to

the soil surface. Pure Kaolinite and Goethite were approximately equal in their effectiveness, with both being half as effective as the soils from Camp Edwards. Desorption experiments showed that tested materials released tungsten in the same relative order as during sorption. The desorption data, however, indicated less release of the sorbed tungsten, indicating that over the 24-hr-experimental time frame, tungsten sorption is not fully reversible. The authors' previous work with similar anions such as  $TCO_4$ -(Clausen et al. 1997; Gu et al. 1994, 1996; Clausen and Early 2002) and  $PO_4$ -(David et al. 2004; AMEC 2002) that behave similarly to  $WO_4$ - suggests that an experiment of longer duration might reveal that tungsten is fully reversible. In summary, relative effectiveness for sorption/desorption (from greatest to least) was:  $Al_2O_3$ , forest soil, Ottawa Sand, MMRBMB022S1, Kaolinite, Goethite.

These results suggest that earlier batch dissolution/desorption tests, previously discussed in Section 4.3.3, primarily contained tungsten metal. In current experiments where soil was spiked with sodium tungstate and desorbed with DI, a low rate of tungsten removal resulted. However, a high percentage of tungsten was observed in the leachate batch dissolution/desorption tests, suggesting that a greater proportion of tungsten metal versus tungstate sorbed to the soil surface was present in contaminated SAR soils.

Xu et al. (2006) present evidence that phosphate either forms more soluble complexes with tungsten or competes for sorption sites, thereby increasing rather than hindering tungsten's mobility. In contrast, phosphate complexes inhibit the mobility of lead. A number of preliminary experiments performed with contaminated soil MMRBMB022S1 showed that when phosphate was added, less sorption occurred; however, the effect was only a few percent. No discernable effect of adding phosphate on desorption was detected. Any conclusions from these data must be tempered with unknown effects of the previous presence of tungsten and the small number of experiments conducted. The percentage of phosphate in the Maectite material used to treat the SAR is unknown, because the Maectite is proprietary material. Nevertheless, when phosphate is added, the remaining tungsten dissolves and sorption may be inhibited for the SAR ranges at Camp Edwards. Conversely, dissolved and subsequently sorbed tungsten may not be affected.

#### 4.4.2 Column testing

Three column experiments were conducted as part of Task 5; two assessed dissolution/desorption of tungsten from a contaminated soil, and a third assessed sorption/desorption/dissolution of aqueous sodium tungstate (Table 12). These tests were conducted to determine how much leachate was generated from a SAR-contaminated soil from either desorption or dissolution processes. Our secondary objective was to determine the proportional difference of the two transport process from the previous batch experiments where each mechanism was studied independently, as described in Section 4.3.

Prior to conducting the experiments, permeability of the columns was determined with a falling-head test. In addition, a chloride tracer test confirmed the uniformity of the column packing and the absence of significant channeling.

Column ID	Treatment Conditions	Cumulative Time (hrs)	Cumulative Pore Volumes	Cumulative Volume (L)
1	Desorption/dissolution of tungsten	451	39	8.1
2	Sorption of sodium tungstate and desorption/dissolution of tungsten and sodium tungstate	124	10.8	2.2
3	Desorption/dissolution of tungsten	50	4.4	4.4

Table 12. Treatment conditions in column experiments.

Each of the three columns was prepared in an identical fashion (Figure 13), using a 61-cm-long glass chromatography column with a 5.0-cm inner diameter made by Ace Glass, Inc. (Catalog #5889-40). The column had a 1-cm permeable glass frit at the base. Above the frit was 2 cm of glass wool and 3 cm (70 g) of 5-mm glass beads, pre-washed with DI, which prevented sediment from clogging the frit. Each column was rinsed several times with DI prior to loading with soil. The columns were dry packed with a 20-cm layer (504 g) of soil. DI was added, and the soil was tamped slightly to eliminate voids.

The gravelly sand soils used in the tests were obtained from Kilo (K) Range at Camp Edwards and were originally designated K6 and K7. When collected, soils had a pH of 7.2 and a moisture content of approximately 20%. The tungsten content of the K6 and K7 soils was 28 and 52 mg/kg, respectively. Differentiation between the metallic species present and the sorbed species of the various metals in the soil was not possible. The remaining

chemical analyses showed the soils (K6/K7): to be very similar: organic carbon content 2.2/2.7%; bulk density 1.3/1.2 g/cm³; cation exchange capacity 16/17 meq/g; aluminum 7260/7,550 mg/kg; barium 22/22 mg/kg; beryllium 0.33/0.33 mg/kg; calcium 15,900/15,400 mg/kg; chromium 600/600 mg/kg; copper 390/240 mg/kg; iron 13,300/13,300 mg/kg; potassium 1,100/1,100 mg/kg; magnesium 1,300/1,480 mg/kg; manganese 120/120 mg/kg; sodium 130/120 mg/kg; nickel 10/9 mg/kg; lead 640/700 mg/kg; vanadium 18/20 mg/kg; and zinc 64/38 mg/kg. The following metals were not detected above the reporting limit: silver, arsenic, cadmium, antimony, and selenium. K7 soil was used in Columns 1 and 2, and a 50:50 mixture of K7 and K6 soil was used in Column 3. The 50:50 mixture was used because there was insufficient K7 material to pack Column 3.

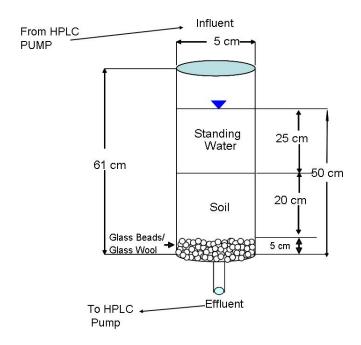


Figure 13. Column design for the study.

A 25-cm head of water was maintained on top of the soil surface. Manual flow control using a stopcock was not effective. Flow was thus controlled by an 8-channel multi-head Cole—Palmer Masterflex L/S HPLC peristaltic pump, Model 7519-06. The flow rate for all columns was 0.3 mL/min, except for Column 3; which used a second Cole—Palmer Masterflex L/S HPLC peristaltic pump, Model 7519-06, at 0.6 ml/min. All columns were wrapped in aluminum foil. The laboratory had no exterior windows and was generally dark except when samples were collected.

Two fraction collectors, either an ISCO Retriever II, Model 69-283-047 or a Spectra-Chrom, Model CF-1, were used when collecting samples at a high frequency. When a high sample frequency was not needed, samples were collected manually.

To determine residence time of one pore volume, the soil volume and soil porosity must be calculated. Soil volume in each column was found to be 392.5 cm<sup>3</sup> by using the equation:

$$V_{\text{soil}} = \pi * r^2 * h$$
 eq. 1

where:

 $V_{soil}$  = volume of soil in the column (cm<sup>3</sup>)

 $\pi = pi (3.1416)$ 

r = radius of the column (2.5 cm)

h =thickness of soil in the column (20 cm).

The porosity of the soil can be calculated using:

$$n = 1 - (\rho_b / \rho_s)$$
 eq. 2}

where:

n =porosity of the soil (unit less)

 $\rho_b$  = bulk density of the soil (1.26 g/cm<sup>3</sup>)

 $\rho_s$  = specific gravity of the soil (2.65 g/cm<sup>3</sup>).

The calculated porosity of the soil is 0.52. Because columns typically cannot be compacted as well as field soil, the porosity of a column experiment is usually higher than a field value. Hence, the value of 52% is higher than for coarse soils at Camp Edwards. The pore volume ( $P_v$ ) of the soil is the volume of soil ( $V_{soil}$ ) times porosity (n), which yields a value of 205.9 cm<sup>3</sup>. The residence time of one pore volume is then calculated using:

$$R_T = (P_V / Q)$$
 eq. 3}

where:

 $R_T$  = residence time of one pore volume (s)

 $P_V$  = pore-volume (205.9 cm<sup>3</sup>)

Q = flow rate through the column (0.3 mL/min or 0.005 mL/s).

Solving for  $R_T$  in equation 3 yields a residence time of one pore volume in the column of 4.12E+4 s or 11.4 hr.

At column start up, a solution of sodium chloride was added, and the chloride acted as tracer for assessment of flow conditions. The salt solution had a chloride concentration of 50~mg/L.

#### 4.4.2.1 Falling-head test

A falling-head permeameter test was conducted on each column to assess the hydraulic conductivity of the soil. The test allows unimpeded flow from the column and measures the change in head over a specified time period. The equation to calculate the hydraulic conductivity is:

$$K = (L * d^2) / (D^2 * t) * In \triangle h$$
 eq. 4

where:

K = hydraulic conductivity (cm/s)

L =length of the soil sample (20 cm)

 $d^2$  and  $D^2$  = diameter of column (5 cm)

t = time (s)

 $\blacktriangle h$  = change in height of water column (cm).

The calculated hydraulic conductivity (Table 13, uncorrected) has to be corrected for changes in viscosity as a function of temperature. The soil temperature was approximately  $17^{\circ}$ C, equating to a correction factor of 1.077, which is based on values reported by Kasenow (2006). The results indicate hydraulic conductivity varied from 5.04 x  $10^{-3}$  cm/s for Column 1 to 2.69 x  $10^{-2}$  cm/s for Column 2, which is a reflection of packing consistency. Some variation in hydraulic conductivity may exist due to differential settling as material was transferred from sample bags to the columns.

Table 13. Falling-head permeameter hydraulic conductivity determinations.

Column	Change in Water Column height- ▲ h (cm) Time (s)		Uncorrected Hydraulic Conductivity (cm/s)	Corrected Hydraulic Conductivity (cm/s)	
1	5.4	7,200	4.68 x 10 <sup>-3</sup>	5.04 x 10 <sup>-3</sup>	
2	3.2	900	2.58 x 10 <sup>-2</sup>	2.69 x 10 <sup>-2</sup>	
3	6.5	1,800	2.08 x 10 <sup>-2</sup>	2.24 x 10 <sup>-2</sup>	

Using information from the current SESOIL model for MMR (Kulbersh; CENAE personal communication), the calculated vertical hydraulic conductivity of the Camp Edwards soil is approximately 3.12E-5 cm/s over the entire 36 m (120 ft) thickness of the unsaturated zone. The depositional lithologic history at Camp Edwards consists of a coarsening upwards sequence. Therefore, soils at or near the surface are expected to have a higher hydraulic conductivity than the average. Additionally, packing the soils in a column as tightly as they occur in nature is nearly impossible, and thus the column conductivity is likely to be higher than for field measurements. Consequently, the measured hydraulic conductivity values for the column experiments are reasonable.

### 4.4.2.2 Tracer experiments

At the start of each column experiment, a tracer test was conducted. Tracer data can be found in Appendix F. Tracer tests were conducted with a conservative trace, chloride, to assess whether the breakthrough curves exhibited plug-type flow, where the tracer concentration has a nearly vertical rise indicative of an advective, dispersive front. The concentration should then plateau near the influent value, and when the tracer is discontinued from the influent, the decline should be almost vertical.

The chloride breakthrough curve for Column 1 shows a more gradual rate of chloride breakthrough, as well as some shouldering instead of a plateau (Figure 14). Most likely, these data are the result of non-uniform pore water velocity rather than sorption of the chloride onto the soil. Non-uniform pore water velocity was probably caused by heterogeneity in the column packing. Column 1 chloride levels reached a plateau near the influent concentration of 50 mg/L in less than 2 days. At approximately 55 hr, the chloride input was discontinued, and the remaining chloride was flushed out within 50 hr or approximately five pore volumes.

The chloride breakthrough curves for Columns 2 and 3 are shown in Figure 15. The Column 3 curve is similar to Column 1. In both columns, the chloride concentration declined rapidly when input was discontinued.

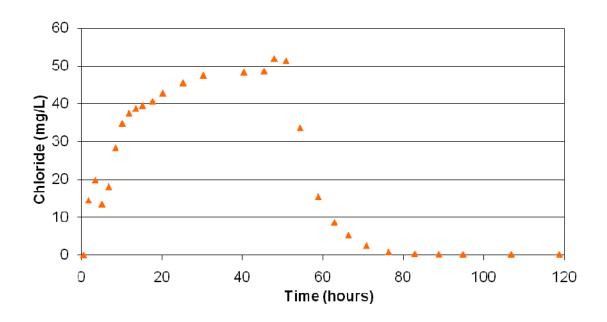


Figure 14. Chloride breakthrough curve for Column 1. Soil concentration is 52 mg/kg tungsten. (Raw data presented in Appendix F).

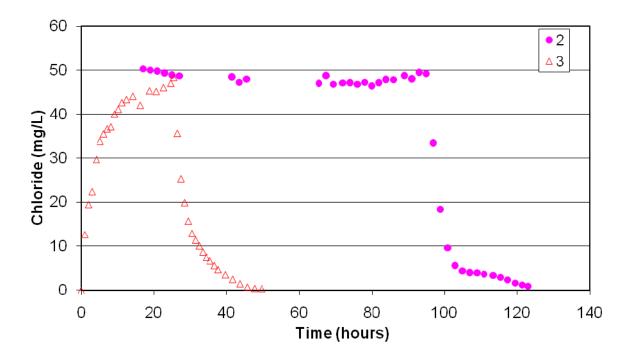


Figure 15. Chloride breakthrough curves for Columns 2 (purple) and 3 (red). (Raw data presented in Appendix F).

#### 4.4.2.3 Leaching experiments

In the Column 1 experiment, soil collected in the field contained 52 mg/kg of tungsten and was leached with 40 pore volumes of DI as previously described. Because soil was obtained from the SAR and exposed to weathering processes, both metallic and sorptive species of tungsten were possibly present. Therefore, leachate generated in this experiment is due to both dissolution and desorption processes. The tungsten concentration in the effluent was initially greater than 0.5 mg/L but quickly leveled off to near 0.15 mg/L (Figure 16; Appendix F). The breakthough was so rapid in all three column tests that initial breakthrough was not captured. Observed leachate concentrations, however, are lower than those obtained from the batch tests (Section 4.3.3) with low tungsten soil levels. If we assume that the release rate of tungsten in the batch experiments is similar to that of the columns, the likely explanation is that greater soil surface area in the columns results in greater re-adsorption of the tungsten intially desorbed from the soil. Equilibrium between the desorption of tungsten from soil into the water appears to occur at approximately five pore volumes.

The Column 2 experiment used the same soil as in Column 1 (52 mg/kg of field-contaminated tungsten). In this case, the influent had a concentration of 10 mg/L sodium tungstate (Figure 17). The concentration in the effluent was relatively stable and remained between approximately 0.3 mg/L and slightly more than 0.4 mg/L. The leachate is the result of both dissolution and dissolution of the tungsten introduced from SAR firing, as well as a lack of desorption or possible sorption and subsequent desorption of the added sodium tungstate. Fluctuations are believed to be partly a result of vascilating flow rates and column pressures. The data demonstrated more than 95% removal of the influent tungsten with no indication that the removal rate changed over the course of the experiment. A decrease in removal rate, i.e higher concentrations, would suggest exhaustion of the sorption sites. These results suggest that soil retains a fairly large capacity to remove tungstate ions through sorption processes. Because of oscillation in leachate concentrations, determination of actual equilibrium achievement times was difficult but appeared to be similar to Column 1 and occured around five pore volumes.

The Column 3 experiment was performed in the same manner as Column 1 in which contaminated soil (a 50:50 mixture of the 52 mg/kg soil and 28 mg/kg soil collected in an adjacent location) was leached with DI. In this case the flow rate was twice as rapid (Figure 18). Concentrations were higher than those at the lower flow rate and varied between approximately

0.4 and 0.6 mg/L. These concentrations were somewhat more than double those of the slower flow rate experiment, suggesting that the degree of sorption as compared to Column 1 was half as much.

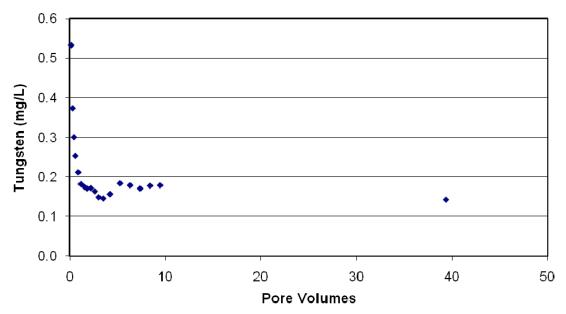


Figure 16. Desorption of tungsten from soil contaminated at 52 mg/kg (Column 1). (Raw data presented in Appendix F).

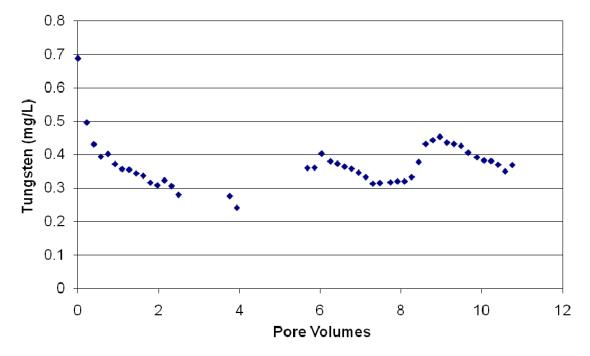


Figure 17. Tungsten in effluent when soil contaminated with 52 mg/kg of tungsten is leached with 10mg/L sodium tungstate (Column 2). (Raw data presented in Appendix F).

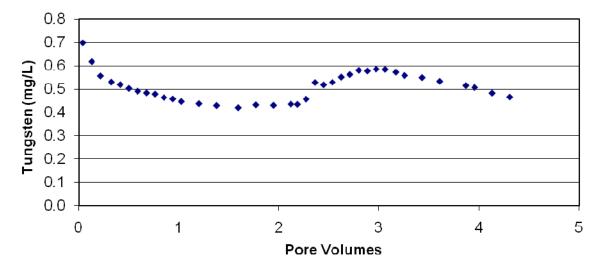


Figure 18. Contaminated soil (50:50 mixture of 52 mg/kg and 28 mg/kg tungsten) leached with DI (Column 3) at ~twice the flow rate of Column 1 experiment. (Raw data presented in Appendix F.)

Reasons why concentrations are higher at a faster flow rate are open to speculation. Batch test data indicated that desorption occurred to a lesser extent than sorption, but such data do not shed light on the reaction rate. Possibly, some tungsten dissolves/desorbs rapidly, and with the faster flow rate, has a lesser opportunity to re-adsorb and is transmitted through the column. Additional and longer experiments would be required to determine the mechanisms with certainty. The implications for Camp Edwards are that high intensity precipitation events likely result in rapid flux of water through the vadose zone, which in turn results in more rapid dissolution of metallic tungsten and desorption of tungsten oxides from the soil surface. When tungsten is mobilized as tungstate, under high-infiltration rate conditions it is re-adsorbed less efficiently. Consequently, tungstate is rapidly transmitted through the vadose zone to the water table. Under low-intensity precipitation, dissolution and desorption of tungsten is likely decreased, and the slower rate of transport through the vadose zone allows for a higher degree of re-adsorption, limiting the amount of tungstate that reaches groundwater.

## 4.5 Task 6 - Unsaturated zone flow modeling

Task 6 consisted of unsaturated zone modeling and used information from Tasks 1 through 5 in order to predict the tungsten transport rate across the approximate 36-m unsaturated zone at Camp Edwards. ERDC-CRREL performed this task using the Seasonal Soil Compartment (SESOIL) model (Bonazountas and Wagner 1984; Hetrick et al. 1993) and the same input

parameters used for previous unsaturated modeling efforts at Camp Edwards to support IAGWSP (Appendix G).

As noted in Section 4.4.1.1, tungsten  $K_d$  values measured in Task 5 ranged from a low of approximately 20 L/kg to a high of approximately 450 L/kg;  $K_d$  increased with contact time up to approximately 60 days or more. The initial modeling step was to predict whether tungsten detected in the soil samples at SARs would impact groundwater. Tungsten predicted to reach groundwater was modeled using the Analytical Transient 1-, 2-, and 3-Dimensional Simulation of Waste Transport in the Aquifer System (AT123D; Yeh 1981) to calculate the concentration in the groundwater. Both models were run using the SEVIEW software program (version 6.3, Environmental Software Consultants 2006). SESOIL was used to predict the time required for migration through the vadose zone, and the AT123D model was used to predict the groundwater concentration at the interface of the unsaturated and saturated zones. Saturated zone modeling is discussed in the next subsection, and the models are explained in more detail in Appendix G.

#### 4.5.1 Unsaturated zone modeling results

With a tungsten soil concentration of 70 mg/kg and a  $K_d$  of 200 L/kg, the SESOIL model predicted tungsten would not migrate more than 1 m below the ground surface (bgs). Increasing the soil concentration to 700 and 7,000 mg/kg had no impact on the predicted depth of migration. Clearly, these simulations seriously underestimated the actual extent of tungsten migration as shown by the sampling of lysimeters and MW-72S on B Range. In order to simulate additional transport, 20 L/g, the lowest  $K_d$  measured in these experiments, was used with an initial soil concentration at 70 mg/kg. This simulation did predict tungsten would reach groundwater, albeit in 700 years. The maximum concentration predicted was 30  $\mu$ g/L. Changing the source-term concentration changed the concentration predicted in groundwater but did not change the transport time. Thus, even with the lowest  $K_d$  measured in this study, the modeling results seriously under predict what was observed in the field.

To better understand why the modeling under predicts tungsten migration, SESOIL simulation was conducted with a  $K_d$  of 1 L/kg, using an initial soil concentration of 70 mg/kg. In this scenario, tungsten reaches the groundwater in 25 years as compared to 6 years. Even with a  $K_d$  of 1 L/kg, 50 years were required before groundwater concentration reached a maximum level of 957  $\mu g/L$ , whereas the maximum tungsten concentration observed at MW-72S was approximately 550  $\mu g/L$ . These results sug-

gest the tungsten observed at MW-72S resulted from a source area having an average soil concentration greater than 70 mg/kg. As noted in Clausen et al. (2007b), tungsten soil concentrations in the berm surface soils at B Range, where MW-72S is located, were 100 to 1,000 mg/kg.

A possible reason that unsaturated zone modeling results are at odds with field observations is that tungsten migration is a more complex phenomena than can be simulated with SESOIL. As observed in the batch experiments (Section 4.3), the degree of tungsten sorption is variable and dependent upon the contact time with the surrounding soil. If infiltration rates are lower, there is a greater degree of tungsten adsorption. As infiltration rates are increased, the efficiency of adsorption decreases. SESOIL can not accommodate variable infiltration rates or  $K_d$  values and does not account for desorption of tungsten from the soil surface and subsequent remobilization. Further column testing would be needed to assess the resulting difference in dissolution and desorption/sorption rates as a function of infiltration rates. Column testing in Section 4.4 suggests higher flow rates result in greater mass of transported tungsten, which would also correspond with a lower associated  $K_d$ .

More importantly, SESOIL assumes the initial release of a contaminant is in a dissolved phase and does not account for dissolution. The SESOIL process of releasing a soil concentration into solution is dependent upon solubility. Although, the solubility of metallic tungsten is unknown, results from field lysimeters (Clausen et al. 2007b) suggest it is at least 400 mg/L. Consequently, SESOIL will allow conversion of a large mass of tungsten to a solute form. However, the amount of tungsten released in solution is going to be a function of precipitation intensity, humidity levels, pH of the precipitation.

Additionally, SESOIL does not account for competitive sorption. At B, C and I Ranges, Maectite, a phosphate-based agent, was used to fix lead in the soil prior to the use of tungsten ammunition. The soil sorption sites, therefore, were loaded with phosphate, which can compete with tungstate (Xu et al. 2006). As a consequence, when tungsten rounds began to be used in training, a limited number of sorption sites were possibly available in the surface soil. In effect, the presence of Maectite lowered the tungsten  $K_{\rm d}$ .

Of serious concern, SESOIL usage is unable to account for the extent of variation in geochemical and hydraulic conditions. The migration of tungsten through the Camp Edwards vadose zone is apparently dependent on several factors that are not easily accommodated by a modeling approach

with strict reliance on  $K_d$ s. The extent that conditions change with soil depth is probably greater than can be addressed with the model. For example, sequences of gravel and cobbles have been reported in the vadose zone (AMEC 2001a). In such locations, water flow is probably so rapid and the substrate surface area is so low that little opportunity exists for attenuation regardless of pH. If these coarse sequences occurred in locations where tungsten was migrating, the average hydraulic conditions, as used in the model, would under predict the flow rate of pore water.

Analogous to other metals that migrate chiefly as oxyanions (e.g. molybdenum and vanadium), tungsten is more mobile under oxidizing conditions. Measurement or simulation of redox conditions as they occur in the field is difficult. Closed vials and columns used to measure  $K_d$  probably do not mimic the subsurface and may actually become more reducing over time. The extent to which redox conditions affect tungsten mobility has not been measured and was not addressed in the model simulations. The subsurface redox conditions at Camp Edwards have been documented in numerous ways, including direct measurements of dissolved oxygen and indirect observations such as the lack of detections of reduced species (AMEC 2001a, 2001b). As observed at Camp Edwards, sandy soil, combined with high rainfall and rapid movement through the vadose zone, are conducive to the maintenance of oxidizing conditions. As with variation in soil texture, the redox environment is not uniform throughout the vadose zone (AMEC 2001a, 2001b).

Finally, tungsten speciation changes with time and geochemical conditions (Bednar et al. 2008). Although polytungstates and tungstate are negatively charged, they are much larger ions and this may decrease their availability to certain sorption sites. For these reasons, SESOIL modeling based on a laboratory-derived  $K_{\rm d}$  and on average hydraulic and geochemical conditions is apparently unreliable for the prediction of tungsten mobility at Camp Edwards.

## 4.6 Task 7 – Saturated zone particle tracking

Paths of ground water originating as recharge at B Range were simulated with the existing USGS regional ground-water flow model developed for MMR using particle tracking. Particle paths were delineated in map view (Figure 19). The original intent was to develop detailed particle tracks for all SARs, with the anticipation that tungsten would likely be present at all ranges where the tungsten/nylon project was used. However, lack of tungsten in groundwater at C and SE/SW Ranges, and lack of an extensive area of contamination at B Range, made detailed particle tracking unnecessary.

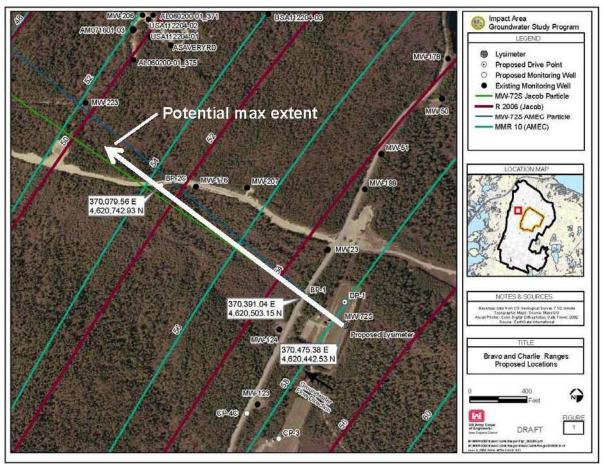


Figure 19. Particle track originating at Bravo Range.

Particle tracks were generated beginning at all SARs where tungsten projectiles were used (Figure 20) in the event that tungsten was identified at the other SAR not studied as part of this activity. These particle tracks represent the general migration path of a contaminant released at the SAR. However, because most ranges had no identifiable zone of tungsten contamination in groundwater, the release pattern is a periodic pulse. Searching for potential contamination, if it exists, would likely fail and be very expensive. Owing to the short period of time (< 6 years) that tungsten projectiles were used, the maximum extent of tungsten in groundwater downgradient can be estimated. The groundwater flow velocity is roughly 0.3m/day (1 ft/day) (AMEC 2001a), yielding a maximum horizontal distance of 2,190 ft. However, as noted in Section 4, the soils at Camp Edwards have a high capacity to adsorb tungsten. Therefore, any tungsten reaching groundwater is likely to be attenuated near the source term, thus limiting its lateral movement in the aquifer. This premise is supported by the drive-point and monitoring wells results for B, C, and SE/SW Ranges, which showed no detectable downgradient presence of tungsten.

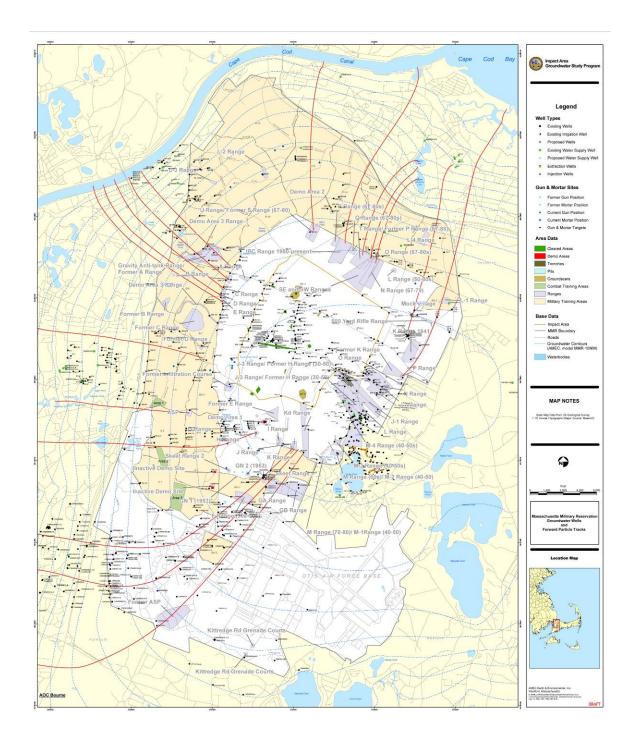


Figure 20. Particle tracks originating at all SARs where tungsten projectiles were used.

# 4.7 Task 8 - Speciation studies

Recently published research is beginning to describe the thermodynamics and kinetics of tungsten phase transformations and mineral associations. This research is in its infancy and currently is more descriptive than quantitative. Tungstate-solution chemistry is complex because, as reported in

Cotton and Wilkinson (1967), "....the alkali metal salts are water soluble... [and]... polymerize ...giving rise to a very complicated series of isopolyanions, the nature of which depends on the circumstances. In the presence of other elements, heteropolyanions can be obtained." The primary objective of the speciation studies was to identify the form of tungsten present in water and provide guidance for future toxicology studies. A secondary objective was to determine what happens to tungsten metal upon release into the environment and to identify the forms of tungsten present on the metal and soil surface after the occurrence of weathering, with the aim of establishing extent and mechanisms of tungsten adsorption to mineral phases present in the soil (Clausen et al. 2007a).

### 4.7.1 Tungsten speciation in water

Tungsten species present in solution at Camp Edwards were studied using a newly-developed analytical technique that separates tungsten species with HPLC, followed by quantification with ICP-MS (Bednar et al. 2007). This method has a detection limit of 0.4 µg/L for tungstate. To determine other species, however, higher concentrations are preferred. The concentrations of poly- and heteropoly-tungstates as a group can only be semi-quantitatively determined with this method because they interact to some extent with the anion exchange column. In addition, resolving the speciation of tungsten requires comparison with analytical standards that are apparently not available for all present species. The only standards available for comparison were for sodium tungstate and polytungstate; the latter is listed as having the following composition:  $Na_6[H_2W_{12}O_{40}]$  or  $3Na_2WO_{4}$ ·+  $9WO_{3}$ ·+  $H_2O$ . Polytungstates can be very complex, and the species in the standard may not be the same as the species in the soil solution.

Figure 21 compares the tungsten response curves for samples collected from lysimeters MMR-21 and MMR-30 against a standard containing polytungstate and tungstate. Lysimeter MMR-21 is located on C Range in the berm face at a depth of 165 cm bgs and was sampled on October 4, 2006 and November 8, 2007.

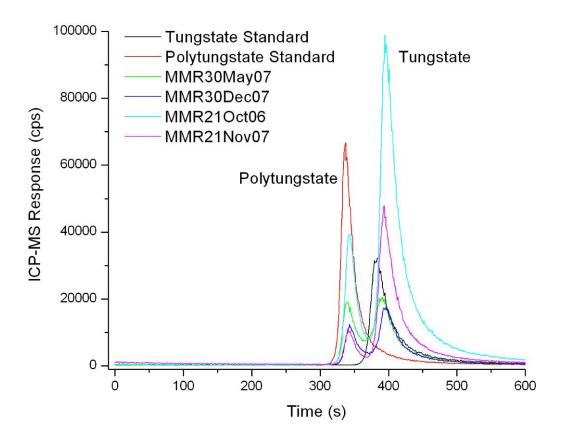


Figure 21. Speciation of tungsten in lysimeter samples from MMR-21 and MMR-30.

MMR-30, located on B Range, was installed on the berm face at a depth of 4.6 m bgs. MMR-30 was sampled on May 30 and December 19, 2007. The response curves for the lysimeter samples compare favorably to the curves for the polytungstate and tungstate standards, indicating both species are present. Reported total tungsten concentrations by ICP can be compared to the tungstate and polytungstate values obtained with HPLC separation (Table 14). The "total" tungsten values by ICP tended to be lower than the tungstate + polytungstate results. At the time of these analyses, the HPLC-ICP-MS method was semi-quantitative, and this caused the concentration differences. Values are sufficiently similar so that overall data interpretation is not affected.

As reported by Clausen et al. (2007b), a sample from monitoring well MW-72S was analyzed for tungsten using the speciation method of Bednar et al (2007). This sample, collected on May 10, 2006, had a reported tungsten concentration of approximately 550  $\mu$ g/L.

Table 14. Total tungsten concentration compared to tungstate and polytungstate in lysimeters MMR-21 and MMR-30.

		Species Concentration (µg/L)				
Lysimeter ID	Sample Date	Total Tungsten (ICP)	Tungstate (SEC-ICP-MS)	Polytungstate (SEC-ICP-MS)	Ratio of Tungstate to Polytungstate	
MMR-21	October 2006	18, 100	30,400	3,600	8:1	
MMR-21	November 2007	10,000	14,100	980	14:1	
MMR-30	May 2007	1,400	1,530	390	4:1	
MMR-30	December 2007	1,400	1,170	230	6:1	

The results for this particular sample indicated a good match with the sodium tungstate standard with polytungstate species not evident. These results suggested tungstate is the predominant species of tungsten migrating at Camp Edwards. The presence of polytungstate in the lysimeter samples shows that polymerization occurs in the vadose zone water. No significant difference exists between tungsate:polytungstate ratios for MMR-21 versus MMR-30; the latter is approximately 3-m deeper than the former. Thus, no appreciable attenuation of polytungstate relative to tungstate occurred over this depth interval. Attenuation of polytungstate relative to tungstate should result in increasing tungstate:polytungstate ratios. Evaluation of water from MW-72S (Figure 22), however, suggests polytungstates may not migrate as readily — a conclusion in agreement with other recently-published research (Bednar et al. 2008) that suggested attenuation occurred between 4.5 m and the water table (36 m).

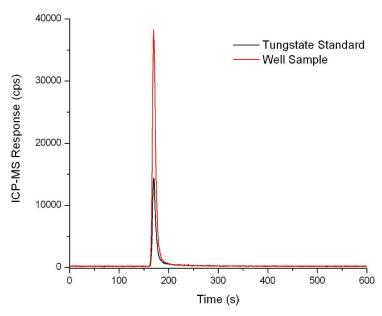


Figure 22. Speciation of tungsten in monitoring well sample MMR-72S.

#### 4.7.2 Tungsten speciation in soil

ERDC/CRREL, in conjunction with Dartmouth College, plans to examine tungsten speciation in soils using synchrotron-based x-ray absorption spectroscopy (XAS). XAS, which is an element-specific probe of molecular structure, can detect trace quantities of specific tungsten species and provide a quantitative measure of their presence in soils and other complex media. XAS is unique in that it can be performed on whole soils without physical or chemical separations that alter speciation. The objective is to establish the extent and mechanisms of tungsten incorporation into stable mineral phases (e.g., tungstate minerals), and tungsten adsorption to mineral phases for which it has a high affinity, such as iron oxides and sulfide minerals. These data can then be used to improve the understanding of tungsten transport and bioavailability in soil systems. Information from this work was completed in February 2009 and will be documented in a separate report.

Preliminary tests suggest that tungsten metal oxidizes rapidly when exposed to the environment, and these oxides are short lived because they are transformed rapidly to tungstate species. In one test, tungsten metal powder was mixed with Camp Edwards' soil, and DI was added to make a slurry. After 24 hr, the water was removed, and the soil and tungsten metal were dried at room temperature for 72 hr and sealed in an airtight jar. XAS analysis of the soil sample indicated no presence of tungsten metal. In less than 1 week, all of the tungsten metal had oxidized.

## **5.0 Conclusions**

Drive-point sampling at the aquifer interface, in addition to sampling and analysis of water from new monitoring wells, demonstrated that cessation of training with tungsten rounds and the subsequent soil removal project, limited the area of tungsten migration to groundwater within the vicinity of MW-72S on B range.

Results from shallow lysimeters ( $< \sim 160$  cm) showed tungsten contamination remains in pore waters, although a weak decreasing trend in concentration is consistently observed. Three deep lysimeters ( $\sim 1.5$  to 7 m) installed at B range revealed that tungsten contamination existed in samples acquired over the entire depth interval. However, tungsten concentration also declined substantially with depth.

Laboratory and field experiments show tungsten dissolution may begin immediately upon exposure to oxidizing water, depending on the surface condition of the tungsten metal. The rate of dissolution under controlled conditions of temperature and water contact in the laboratory was relatively constant throughout the course of the experiment. The experiment demonstrated that mg/L concentrations of tungsten could be transferred to percolating waters in a matter of hours. Because of variations in temperature and rainfall, field dissolution was not as consistent but periodically supported the occurrence of rapid dissolution.

Batch experiments with six soils from Camp Edwards showed that  $K_ds$  ranged from approximately 20 to more than 450 mL/g. These findings are consistent with other recently published values, as was the conclusion that tests of 60 days or more were typically necessary to obtain a steady-state result. Sorption/desorption experiments with a variety of substrates and field-contaminated soil all demonstrated that desorption is less than sorption. Column studies with a contaminated soil (tungsten content  $\sim 52$  mg/kg) showed some release of tungsten when leached with DI. The same soil, however, showed little or no loss of ability to remove sodium tungstate from a 10 mg/L influent solution. While these soils have substantial ability to remove tungsten, a small fraction remains mobile. Increasing the infiltration rate, as demonstrated in the column tests, will increase the amount of tungstate migrating through the soil and decrease the amount

sorbed. Under low infiltration, tungsten is greatly attenuated with little reaching groundwater.

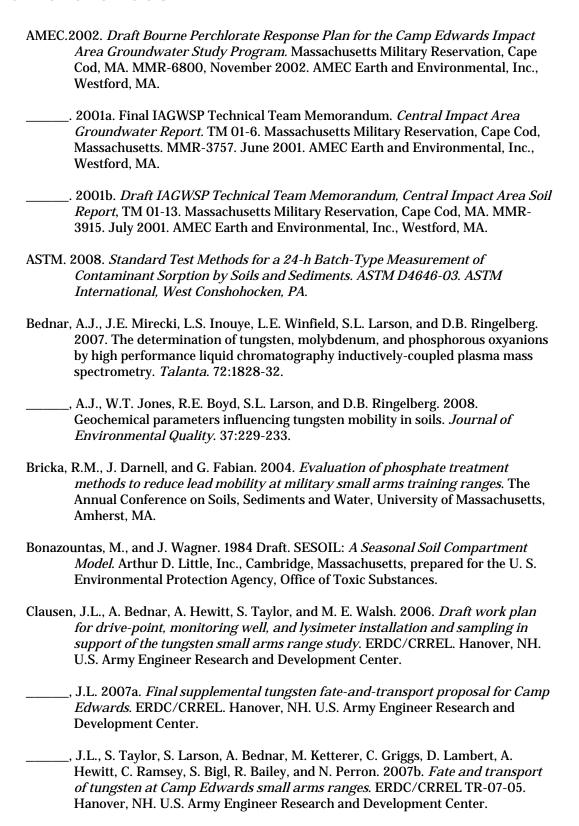
Preliminary speciation studies showed that both tungstate and polytung-state(s) are present in the soil pore water at Camp Edwards, indicating the polymerization of tungstate. However, tungstate is the only species observed in groundwater. Tungsten migration appears to be somewhat controlled by a complex speciation pattern, which is probably dependent on pH, redox conditions, and time. For these reasons, unsaturated zone modeling using SESOIL and laboratory-generated partition coefficients ( $K_d$ s) did not mimic the mobility of tungsten as observed in lysimeters and monitoring wells.

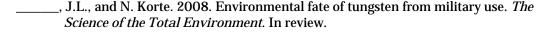
The conceptual model for tungsten that is introduced into the environment as a result of training with tungsten/nylon projects at SARs is described as follows. Upon impact, the metallic tungsten/nylon round breaks up into micron-sized particles that are deposited upon the soil surface. Under windy conditions some tungsten particles may be deposited tens of feet from the berm face. Almost immediately, tungsten metal is oxidized, i.e. it rusts. Precipitation washes portions of tungsten oxides from the tungsten metal surface through a dissolution process and transports them in the form of tungstate. Some portion of the tungstate polymerizes in the vadose zone to form polytungstate species. In soils with low phosphate content, the tungstate/polytungstate is sorbed onto the soil surface. The greater length of time that tungstate is in contact with the soil surface results in a greater quantity of adsorbed tungstate and polytungstate; which is a function of the intensity of the precipitation event and resulting infiltration rate. Low-intensity precipitation events result in less tungsten dissolution and thus a lower rate of tungstate formation. Additionally, the infiltration rate is lower, causing longer contact time, which results in greater tungstate/polytungstate sorption as quantified by increasing K<sub>d</sub> values. However, tungstate is also readily desorbed from the soil surface although the reaction is not completely reversible; some tungstate/polytungstate is retained on the soil surface. In locations with high soil phosphate content, the sorption sites are filled and limit the sorption of tungstate/polytungstate onto the soil surface. The presence of metal oxides such as aluminum increases the amount of tungstate and, presumably, polytungstate sorbed onto the soil. Tungstate that is not sorbed onto the soil migrates with water through the unsaturated zone. Polytungstate appears to be completely sorbed within the vadose zone. Tungstate moves

in the direction of water flow when reaching the groundwater table. The concentration of tungsten that reaches groundwater will be a function of the initial tungsten soil mass and the area over which it is deposited. Upon reaching groundwater, tungstate continues to be attenuated due to sorption processes, thus limiting its lateral migration. Tungstate reaches groundwater only under high-intensity precipitation events, resulting in a pulse-type release pattern. Consequently, tungstate concentrations from a fixed point in groundwater, such as a monitoring well, swing back and forth from relatively low levels (1 to 20  $\mu g/L$ ) to high levels (hundreds of  $\mu g/L$ ), relatively quickly (days to weeks). This pulse pattern of release will result in small groundwater areas with elevated tungsten, sandwiched between zones of lower concentrations. Therefore, the area of groundwater contamination is likely to be discontinuous in nature, making detection difficult.

In summary, various field data and laboratory experiments demonstrate that tungsten from training rounds rapidly oxidizes and dissolves in percolating waters to form tungstate and polytungstate species. Sampling of numerous groundwater wells has shown that background concentrations are less than the 1  $\mu g/L$  reporting limit. Any tungsten reported in groundwater and pore-water samples is therefore a result of oxidation, dissolution, and leaching from anthropgenically-derived sources.

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# Appendix A. Groundwater Monitoring Wells Sampled

Table A-1. Existing IAGWSP wells analyzed by ERDC-EL in Phase I tungsten SAR study.

SAR Wells	Background Wells
MW-72S (on B Range)	MW-135M1
MW-123M1 (downgradient of B and C Range)	MW-404S

Data for these wells has been previously provided in Clausen et al. (2007b), with additional Phase II ERDC-EL data provided in Table 2 of this report. These wells were sampled for the IAGWSP with sample splits provided to ERDC-EL and analyzed as part of the Tungsten SAR Study. STL-generated data is not provided in this report but is available from CENAE/IAGWSP.

Table A-2. Existing IAGWSP wells sampled to measure background.

We	ell ID
MW-05M2	MW-151S
MW-07M2	MW-254M2
MW-62S	MW-280M2
MW-67S	MW-357S
MW-71M1	MW-404S
MW-79M2	

These wells were sampled by ECC for CENAE/IAGWSP and analyzed by STL with split samples provided to NAU. NAU analysis was conducted as an activity under the Tungsten SAR Study. The NAU data is provided in this report in Table 4. Additional analytical results are not provided in this report but are available from CENAE/IAGWSP.

Table A-3. Tungsten SAR study phase II wells.

Range	Well ID
B Range	MW-455S
Ditalige	MW-490S
C Range	MW-491S
Ortange	MW-456S
SE Range	MW-465S
or name	MW-466S
Tango Range	MW-467S

These wells were installed for ERDC-EL by CENAE for the Tungsten SAR Study. Wells were sampled by ECC for CENAE with split samples provided to ERDC-EL. The ERDC-EL analyses were conducted as a part of the Tungsten SAR Study. The ERDC-EL data are provided in Table 6 of this report.

## **Appendix B. Results from Drive-Point Sampling**

(Notes available at end of Table)

Range	Sample Number DP-	Date Sampled	Top Depth (ft)	Bot Dept h (ft)	Filt./ Unfil	ERDC W¹ µg/L	NAU W¹ µg/L	V µg/L	Cr µg/L	Mn μg/L	Fe µg/L	Ni µg/L	Cu µg/L	Zn ug/L	As ug/L	Se ug/L	Mo ug/L	Sb ug/L	Pb ug/L
В	443 (DP-01)-01	8/14/2006	112.1	114.6	F	<0.5	<15 1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	443 (DP-01)-01	8/14/2006	112.1	114.6	F	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
B <sup>3</sup>	443 (DP-01)-01	8/14/2006	112.1	114.6	F2X	NA	<0.3 <sup>2</sup>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	443 (DP-01)-01	8/14/2006	112.1	114.6	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	443 (DP-01)-01	8/14/2006	112.1	114.6	F	NA	NA	<1	1.7	523	3754	42.2	6.8	4194	2.4	2.2	26	2.2	2.0
В	443 (DP-01)-01	8/14/2006	112.1	114.6	F	NA	NA	<1	1.7	519	NR	42.8	6.7	4121	1.8	1.7	26	1.6	2.0
В	443 (DP-01)-01	8/14/2006	112.1	114.6	U	NA	NA	1	63	260	14590	46.3	79	4214	4.5	2.5	25	1.9	1.1
В	443 (DP-01)-02	8/14/2006	114.6	119.6	F	<0.5	<15 <sup>1</sup>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
B <sup>3</sup>	443 (DP-01)-02	8/14/2006	114.6	119.6	F2X	NA	<0.3 <sup>2</sup>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	443 (DP-01)-02	8/14/2006	114.6	119.6	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	443 (DP-01)-02	8/14/2006	114.6	119.6	F	NA	NA	<1	<1	756	1783	54.4	2.4	3142	1.4	1.5	16	1.2	<1
В	443 (DP-01)-02	8/14/2006	114.6	119.6	U	NA	NA	1.3	52	629	17691	66.6	102	4412	5.2	2.2	30	1.3	3.0
В	443 (DP-01)-03	8/15/2006	119.6	124.6	F	<0.5	<15 1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
B <sup>3</sup>	443 (DP-01)-03	8/15/2006	119.6	124.6	F2X	NA	<0.3 <sup>2</sup>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	443 (DP-01)-03	8/15/2006	119.6	124.6	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	443 (DP-01)-03	8/15/2006	119.6	124.6	F	NA	NA	<1	<1	206	2102	13.2	1.5	368	<1	2	4	<1	<1
В	443 (DP-01)-03	8/15/2006	119.6	124.6	J	NA	NA	<1	6.4	204	7026	18.5	14.8	710	1.2	1.4	9.3	<1	<1
В	443 (DP-01)-04	8/15/2006	124.6	129.6	F	<0.5	<15 <sup>1</sup>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
B <sup>3</sup>	443 (DP-01)-04	8/15/2006	124.6	129.6	F2X	NA	<0.32	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	443 (DP-01)-04	8/15/2006	124.6	129.6	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	443 (DP-01)-04	8/15/2006	124.6	129.6	F	NA	NA	<1	<1	74	1161	7.4	4.5	364	<1	1.5	2.9	<1	<1
В	443 (DP-01)-04	8/15/2006	124.6	129.6	U	NA	NA	<1	5.7	117	3621	12.7	17	834	1.3	1.5	7	<1	<1

Range	Sample Number DP-	Date Sampled	Top Depth (ft)	Bot Dept h (ft)	Filt./ Unfil	ERDC W¹ µg/L	NAU W¹ µg/L	V μg/L	Cr µg/L	Mn μg/L	Fe µg/L	Ni µg/L	Cu µg/L	Zn ug/L	As ug/L	Se ug/L	Mo ug/L	Sb ug/L	Pb ug/L
SW	444 (DP-02)-01	8/1/2006	138.1	140.1	F	0.6 J	0.53 J	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	444 (DP-02)-01	8/1/2006	138.1	140.1	U	1.1	91 J <sup>1</sup>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW <sup>3</sup>	444 (DP-02)-01	8/1/2006	138.1	140.1	U	1.1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	444 (DP-02)-01	8/1/2006	138.1	140.1	F	NA	<15 <sup>2</sup>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	444 (DP-02)-01	8/1/2006	138.1	140.1	F	NA	NA	< 2	< 2	340	160	113	16.2	1260	3.4	<2	406	4.0	< 2
SW <sup>3</sup>	444 (DP-02)-01	8/1/2006	138.1	140.1	F	NA	NA	< 2	< 2	331	162	114	15.8	1300	3.4	<2	397	4.0	< 2
SW	444 (DP-02)-01	8/1/2006	138.1	140.1	U	NA	NA	5.2	428	1628	122810	1296	2788	243280	75	9.6	265	3.9	4.1
SW	444 (DP-02)-02	8/3/2006	140.6	145.6	F	<0.5	4.3 1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW <sup>3</sup>	444 (DP-02)-02	8/3/2006	140.6	145.6	F2X	NA	<3.02	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	444 (DP-02)-02	8/3/2006	140.6	145.6	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	444 (DP-02)-02	8/3/2006	140.6	145.6	F	NA	NA	<2	< 2	308	431	48	2.6	1890	<2	<2	108	< 2	< 2
SW	444 (DP-02)-02	8/3/2006	140.6	145.6	U	NA	NA	5.4	1419	1759	296470	888	1340	62200	39	3.5	344	14	< 2
SW	444 (DP-02)-03	8/3/2006	145.6	150.6	F	<0.5	<15 <sup>1</sup>	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW <sup>3</sup>	444 (DP-02)-03	8/3/2006	145.6	150.6	F2X	NA	<3.02	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	444 (DP-02)-03	8/3/2006	145.6	150.6	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	444 (DP-02)-03	8/3/2006	145.6	150.6	F	NA	NA	<2	<2	136	126	29	3.3	1540	<2	<2	7.1	< 2	<2
SW	444 (DP-02)-03	8/3/2006	145.6	150.6	U	NA	NA	2.3	426	532	120870	225	368	13170	13.2	<2	123	4.7	<2
SW	447 (DP-05)-01	8/18/2006	136.3	138.8	F	<0.5	<0.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	447 (DP-05)-01	8/18/2006	136.3	138.8	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	447 (DP-05)-01	8/17/2006	136.3	138.8	F			<1	<1	1346	<100	294	13.6	4045	1.2	2.1	71	1.1	<1
SW	447 (DP-05)-01	8/17/2006	136.3	138.8	U	NA	NA	9.6	2703	2941	565691	1618	1913	72173	60	8.7	824	24	1.6
SW	447 (DP-05)-02	8/21/2006	138.8	143.8	F	<0.5	<0.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	447 (DP-05)-02	8/21/2006	138.8	143.8	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	447 (DP-05)-02	8/21/2006	138.8	143.8	F	NA	NA	<1	<1	843	339	111	2.9	1179	1.3	3.5	12	<1	<1
SW	447 (DP-05)-02	8/21/2006	138.8	143.8	U	NA	NA	2.9	542	1125	139656	394	554	16639	8.9	3.8	95	2.9	<1
SW	447 (DP-05)-03	8/23/2006	143.8	148.8	F	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Range	Sample Number DP-	Date Sampled	Top Depth (ft)	Bot Dept h (ft)	Filt./ Unfil	ERDC W <sup>1</sup> µg/L	NAU W¹ µg/L	V µg/L	Cr µg/L	Mn μg/L	Fe µg/L	Ni µg/L	Cu µg/L	Zn ug/L	As ug/L	Se ug/L	Mo ug/L	Sb ug/L	Pb ug/L
SW	447 (DP-05)-03	8/23/2006	143.8	148.8	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SW	447 (DP-05)-03	8/23/2006	143.8	148.8	F	NA	NA	<1	<1	585	93	107	<1	2674	1.3	2.5	9.5	<1	<1
SW	447 (DP-05)-03	8/23/2006	143.8	148.8	U	NA	NA	7.1	712	1022	139138	366	515	14331	11.6	3.8	147	4.4	50
SE	448 (DP-06)-01	8/24/2006	136.5	139	F	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SE	448 (DP-06)-01	8/24/2006	136.5	139	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SE	448 (DP-06)-01	8/24/2006	136.5	139	F	NA	NA	<1	<1	351	54	59	2.8	5160	2.3	1.9	47	<1	<1
SE <sup>3</sup>	448 (DP-06)-01	8/24/2006	136.5	139	F	NA	NA	<1	<1	352	46	58	2.5	NR	2.1	2.0	48	<1	<1
SE	448 (DP-06)-01	8/24/2006	136.5	139	U	NA	NA	3.1	443	1122	103370	527	884	81518	40	7.0	179	7.5	<1
SE	448 (DP-06)-02	8/25/2006	139	144	F	<0.5	<0.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SE <sup>3</sup>	448 (DP-06)-02	8/25/2006	139	144	F	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SE	448 (DP-06)-02	8/25/2006	139	144	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SE	448 (DP-06)-02	8/25/2006	139	144	F	NA	NA	<1	<1	440	107	76	5.0	1503	2.0	<1	79	3.0	<1
SE <sup>3</sup>	448 (DP-06)-02	8/25/2006	139	144	F	NA	NA	<1	<1	442	110	77	4.0	1544	1.0	<1	79	2.0	<1
SE	448 (DP-06)-02	8/25/2006	139	144	U	NA	NA	4.0	440	1552	92453	537	969	67270	23	5.0	76	4.0	3.0
SE	448 (DP-06)-03	8/25/2006	144	149	F	<0.5	<0.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SE	448 (DP-06)-03	8/25/2006	144	149	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SE	448 (DP-06)-03	8/25/2006	144	149	F	NA	NA	<1	<1	401	186	94	8.0	3008	2	<1	41	2.0	<1
SE	448 (DP-06)-03	8/25/2006	144	149	U	NA	NA	6.0	806	1049	117295	483	897	55241	30	4.0	169	7.0	3.0
SE <sup>2</sup>	448 (DP-06)-03	8/25/2006	144	149	F	<0.5	<0.7 J	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SE <sup>2</sup>	448 (DP-06)-03	8/25/2006	144	149	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SE <sup>2</sup>	448 (DP-06)-03	8/25/2006	144	149	F	NA	NA	<1	1.0	361	191	77	5.0	3203	2.0	1.0	44	1.0	<1
SE <sup>2</sup>	448 (DP-06)-03	8/25/2006	144	149	U	NA	NA	5.0	732	1011	116416	473	887	55600	30	3.0	157	6.0	3.0
В	458 (DP-08)-01	8/10/2006	119.6	121.6	F	<0.5	<0.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	458 (DP-08)-01	8/10/2006	119.6	121.6	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	458 (DP-08)-01	8/10/2006	119.6	121.6	F	NA	NA	<1	<1	518	273	79	8.2	6028	1.8	<1	23	1.3	<1
В	458 (DP-08)-01	8/10/2006	119.6	121.6	U	NA	NA	1.8	327	1055	80141	421	935	51836	23	5.7	91	3	2.7
В	458 (DP-08)-02	8/10/2006	122.1	127.1	F	<0.5	<0.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Range	Sample Number DP-	Date Sampled	Top Depth (ft)	Bot Dept h (ft)	Filt./ Unfil	ERDC W¹ µg/L	NAU W¹ µg/L	V µg/L	Cr µg/L	Mn μg/L	Fe µg/L	Ni µg/L	Cu µg/L	Zn ug/L	As ug/L	Se ug/L	Mo ug/L	Sb ug/L	Pb ug/L
В	458 (DP-08)-02	8/10/2006	122.1	127.1	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	458 (DP-08)-02	8/10/2006	122.1	127.1	F	NA	NA	<1	<1	898	<100	163	6.1	7371	2	3.7	27	1	<1
В	458 (DP-08)-02	8/10/2006	122.1	127.1	U	NA	NA	1.4	337	1321	94046	424	826	40052	18.4	5.6	50	2.2	1.6
В	458 (DP-08)-03	8/11/2006	127.1	132.1	F	<0.5	<0.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	458 (DP-08)-03	8/11/2006	127.1	132.1	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
В	458 (DP-08)-03	8/11/2006	127.1	132.1	F	NA	NA	<1	<1	788	660	95	3	4634	1.9	2.5	14.7	<1	<1
В	458 (DP-08)-03	8/11/2006	127.1	132.1	U	NA	NA	2.2	415	1495	123144	395	662	28471	16	4.1	86	3.7	4.4
	EQUIP BLANK	7/31/2006	0	0	U	<0.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	EQUIP BLANK	7/31/2006	0	0	U	NA	NA	<2	<2	5.4	132	<2	2.1	25	<2	<2	2.3	<2	<2

Notes: J - estimated value, NA - not analyzed.

<sup>&</sup>lt;sup>1</sup> The reported <0.3 and <0.5 values are the detection limit for tungsten and not the reporting limit of <1 ug/L. All other reported <x metal values are the reporting limits.

<sup>&</sup>lt;sup>2</sup> Field duplicate.

<sup>&</sup>lt;sup>3</sup> Laboratory duplicate.

#### **Appendix C. Metal and Field Parameter Results for Deep Lysimeters**

Table C-1. ERDC-EL metal results for lysimeters #30, 31, and 32

Lysimeter	Sample Date	W (mg/L)	Ag (mg/L)	Ba (mg/L)	Cd (mg/L)	Pb (mg/L)	Cr (mg/L)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)	Fe (mg/L)	Mn (mg/L)	Mo (mg/L)	V (mg/L)	Sb (mg/L)	As (mg/L)	Se (mg/L)
	11/3/06	0.066	<0.001	0.1713	<0.001	0.0023	0.0016	0.0636	0.0196	0.3243	<0.020	0.2894	0.0259	0.0062	0.0043	0.0038	<0.001
	2/28/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
30	5/30/07	1.436	<0.004	<0.004	<0.004	0.02	<0.004	0.044	0.007	0.097	0.24	0.025	0.009	0.014	0.025	0.009	<0.004
30	8/27/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	11/8/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	12/19/07	1.432	<0.002	<0.002	<0.002	0.012	<0.002	0.022	0.004	0.089	0.020	0.012	0.005	0.014	0.025	0.010	<0.002
	11/3/06	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	2/28/07	<0.002	<0.002	0.030	0.014	0.012	0.007	0.250	0.687	3.271	1.172	21.642	<0.002	0.004	<0.002	<0.002	0.008
31	5/30/07	0.0041	0.046	<0.004	0.015	0.025	0.021	0.176	0.749	3.8	2.047	19.871	<0.004	0.009	<0.004	<0.004	0.012
31	8/27/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	11/8/07	<0.002	0.299	<0.002	0.019	0.023	<0.002	0.015	0.035	0.222	<0.002	1.127	<0.002	<0.002	<0.002	<0.002	<0.002
	12/19/07	<0.002	0.015	<0.002	0.016	0.017	<0.002	0.009	0.032	0.193	<0.002	0.943	<0.002	<0.002	<0.002	<0.002	<0.002
	11/3/06	0.108	0.0029	0.093	<0.001	<0.001	0.0085	0.2076	0.0388	0.3547	<0.020	1.2753	0.0238	0.0154	0.0062	<0.001	<0.001
	2/28/07	0.037	0.002	0.081	0.004	0.021	0.003	0.076	0.181	1.132	1.422	5.271	0.011	0.010	0.007	<0.002	0.004
32	5/30/07	0.0129	0.049	<0.004	0.008	0.044	0.004	0.258	0.338	2.473	2.888	7.099	<0.004	0.007	<0.004	<0.004	0.006
32	8/27/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	11/8/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	12/19/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW

NW - no water.

Table C-2. ERDC-EL field parameter results for lysimeters #30, 31, and 32.

Lysimeter	Sample Date	Sodium (mg/L)	Potassium (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	Phosphate - Phosphorous (mg/L)	Sulfur (mg/L)	Temperature (°C)	Spec. Cond (us/cm)	Total Dissolved Solids (mg/L)	рН	Oxidation Reduction Potential (mv)
	11/3/06	22.8	6.52	2.96	37.8	13.2	15.9	8.4	387	253	6.44	185
	2/28/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
30	5/30/07	NA	NA	NA	NA	NA	NA	16.8	1727	112	4.11	421
30	8/27/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	11/8/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	12/19/07	NA	NA	NA	NA	NA	NA	6.16	131	85	4.81	302
	11/3/06	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	2/28/07	NA	NA	NA	NA	NA	NA	IV	809	NA	4.52	357
31	5/30/07	NA	NA	NA	NA	NA	NA	IV	703	460	4.40	354
31	8/27/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	11/8/07	NA	NA	NA	NA	NA	NA	IV	IV	IV	IV	IV
	12/19/07	NA	NA	NA	NA	NA	NA	6.94	1,804	1,175	3.04	394
	11/3/06	43.6	8.22	8.09	105	< 1	58.3	7.2	880	571	6.49	184
	2/28/07	NA	NA	NA	NA	NA	NA	7.2	1325	NA	5.40	363
32	5/30/07	NA	NA	NA	NA	NA	NA	IV	IV	IV	IV	IV
32	8/27/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	11/8/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW
	12/19/07	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW

IV - insufficient volume for analysis; NA - not analyzed; NW - no water.

## **Appendix D. Results of Sorption Partitioning Over Time**

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Table D-1. Day 1 results – K<sub>d</sub> experiments.

Soil	Sample			Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression Ou	ıtput	K <sub>d</sub>
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorben (kg)	t				
1A	1	115	12	0.01	0.12	11.5	5432	60.680	0.7350	1.7830	Constant	1.2449	18
	2	115	24	0.012	0.12	23	15387	76.130	1.1872	1.8816	Std Err of Y Est	0.1801	
	3	115	60	0.012	0.12	57.5	44848	126.520	1.6517	2.1022	r <sup>2</sup>	0.8207	
	4	115	120	0.012	0.12	115	78392	366.080	1.8943	2.5636	No. of Observations	4	_
			•			•					Degrees of Freedom	2	
											X Coefficient(s)	0.6128	
											Std Err of Coef	0.2025	
1B	1	115	12	0.012	0.12	11.5	5233	62.670	0.7188	1.7971	Constant	1.2751	19
	2	115	24	0.012	0.12	23	15882	71.180	1.2009	1.8524	Std Err of Y Est	0.1961	
	3	115	60	0.012	0.12	57.5	45241	122.590	1.6555	2.0885	r <sup>2</sup>	0.7823	
	4	115	120	0.012	0.12	115	79454	355.460	1.9001	2.5508	No. of Observations	4	
			•			•					Degrees of Freedom	2	
											X Coefficient(s)	0.5823	
											Std Err of Coef	0.2172	
1C	1	115	12	0.012	0.12	11.5	5491	60.090	0.7397	1.7788	Constant	1.208	16
	2	115	24	0.012	0.12	23	15184	78.160	1.1814	1.8930	Std Err of Y Est	0.1736	
	3	115	60	0.012	0.12	57.5	43811	136.890	1.6416	2.1364	r <sup>2</sup>	0.8453	
	4	115	120	0.012	0.12	115	75878	391.220	1.8801	2.5924	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.6557	
											Std Err of Coef	0.1983	

Table D-1 (cont.) Day 1 results - K<sub>d</sub> experiments.

Soil	Sample			Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbe (mg)/ Wt. Sorbent					
2A	1	115	12	0.012	0.12	11.5	4182	73.180	0.6214	1.8644	Constant	1.5175	33
	2	115	24	0.012	0.12	23	13872	91.280	1.1421	1.9604	Std Err of Y Est	0.1505	
	3	115	60	0.012	0.12	57.5	44323	131.770	1.6466	2.1198	r <sup>2</sup>	0.8128	
	4	115	120	0.012	0.12	115	82707	322.930	1.9175	2.5091	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.4474	
											Std Err of Coef	0.1505	
2B	1	115	12	0.012	0.12	11.5	3681	78.190	0.5660	1.8932	Constant	1.6255	42
	2	115	24	0.012	0.12	23	12453	105.470	1.0953	2.0231	Std Err of Y Est	0.1454	
	3	115	60	0.012	0.12	57.5	44395	131.050	1.6473	2.1174	r <sup>2</sup>	0.7955	
	4	115	120	0.012	0.12	115	83168	318.320	1.9200	2.5029	No. of Observations	4	
							•	•			Degrees of Freedom	2	
											X Coefficient(s)	0.3891	
											Std Err of Coef.	0.1395	
2C	1	115	12	0.012	0.12	11.5	3503	79.970	0.5444	1.9029	Constant	1.5956	39
	2	115	24	0.012	0.12	23	13504	94.960	1.1305	1.9775	Std Err of Y Est	0.1572	
	3	115	60	0.012	0.12	57.5	43041	144.590	1.6339	2.1601	r <sup>2</sup>	0.7945	
	4	115	120	0.012	0.12	115	80565	344.350	1.9061	2.5370	No. of Observa- tions	4	
											Degrees of Free- dom	2	
											X Coefficient(s)	0.4209	]
											Std Err of Coef.	0.1514	

Table D-1 (cont.) Day 1 results - K<sub>d</sub> experiments.

Soil	Sample		,	Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	K <sub>d</sub>
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
5A	1	115	12	0.012	0.12	11.5	1221	102.790	0.0867	2.0120	Constant	1.9485	89
	2	115	24	0.012	0.12	23	4241	187.590	0.6275	2.2732	Std Err of Y Est	0.046	
	3	115	60	0.012	0.12	57.5	19083	384.170	1.2806	2.5845	r <sup>2</sup>	0.9896	
	4	115	120	0.012	0.12	115	42772	722.280	1.6312	2.8587	No. of Observations	4	
			'	•		•					Degrees of Freedom	2	
											X Coefficient(s)	0.5335	
											Std Err of Coef.	0.0367	
5B	1	115	12	0.012	0.12	11.5	1219	102.810	0.0860	2.0120	Constant	1.9516	89
	2	115	24	0.012	0.12	23	4169	188.310	0.6200	2.2749	Std Err of Y Est	0.0437	
	3	115	60	0.012	0.12	57.5	19007	384.930	1.2789	2.5854	r <sup>2</sup>	0.9906	
	4	115	120	0.012	0.12	115	42951	720.490	1.6330	2.8576	No. of Observations	4	
											Degrees of Freedom	2	-
											X Coefficient(s)	0.5317	
											Std Err of Coef.	0.0367	
5C	1	115	12	0.012	0.12	11.5	1218	102.820	0.0856	2.0121	Constant	1.9538	90
	2	115	24	0.012	0.12	23	4168	188.320	0.6199	2.2749	Std Err of Y Est	0.0415	
	3	115	60	0.012	0.12	57.5	19172	383.280	1.2827	2.5835	r <sup>2</sup>	0.9914	
	4	115	120	0.012	0.12	115	43835	711.650	1.6418	2.8523	No. of Observations	4	
											Degrees of Freedom	2	-
											X Coefficient(s)	0.5255	1
											Std Err of Coef.	0.0346	]

Soil	Sample			Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression O	utput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
6A	1	115	12	0.012	0.12	11.5	147	113.530	-0.8327	2.0551	Constant	2.3226	210
	2	115	24	0.012	0.12	23	1182	218.180	0.0726	2.3388	Std Err of Y Est	0.0177	
	3	115	60	0.012	0.12	57.5	11707	457.930	1.0684	2.6608	r <sup>2</sup>	0.9984	
	4	115	120	0.012	0.12	115	40638	743.620	1.6089	2.8714	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.3315	
											Std Err of Coef.	0.0095	
6B	1	115	12	0.012	0.12	11.5	162	113.380	-0.7905	2.0545	Constant	2.2989	199
	2	115	24	0.012	0.12	23	1571	214.290	0.1962	2.3310	Std Err of Y Est	0.032	
	3	115	60	0.012	0.12	57.5	12143	453.570	1.0843	2.6566	r <sup>2</sup>	0.9946	
	4	115	120	0.012	0.12	115	41862	731.380	1.6218	2.8641	No. of Observations	4	
			1								Degrees of Freedom	2	
											X Coefficient(s)	0.3365	
											Std Err of Coef.	0.0175	
6C	1	115	12	0.012	0.12	11.5	176	113.240	-0.7545	2.0540	Constant	2.3126	205
	2	115	24	0.012	0.12	23	1130	218.700	0.0531	2.3398	Std Err of Y Est	0.0081	
	3	115	60	0.012	0.12	57.5	11408	460.920	1.0572	2.6636	r <sup>2</sup>	0.9997	
	4	115	120	0.012	0.12	115	42576	724.240	1.6292	2.8599	No. of Observations	4	
			1								Degrees of Freedom	2	
											X Coefficient(s)	0.3359	
											Std Err of Coef.	0.0044	

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Table D-2. Day 30 results - K<sub>d</sub> experiments.

Soil	Sample			Tungstate	•		X axis	Y axis	Log x axis	Log y axis	Regression O	utput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
1A	1	115	12	0.01	0.12	11.5	949	105.510	-0.0227	2.0233	Constant	2.0796	120
	2	115	24	0.012	0.12	23	5188	178.120	0.7150	2.2507	Std Err of Y Est	0.0753	
	3	115	60	0.012	0.12	57.5	39566	179.340	1.5973	2.2537	r²	0.7416	
	4	115	120	0.012	0.12	115	95705	192.950	1.9809	2.2854	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.1158	
											Std Err of Coef.	0.0484	
1B	1	115	12	0.012	0.12	11.5	1191	103.090	0.0759	2.0132	Constant	2.0635	116
	2	115	24	0.012	0.12	23	6202	167.980	0.7925	2.2253	Std Err of Y Est	0.0894	
	3	115	60	0.012	0.12	57.5	38422	190.780	1.5846	2.2805	r <sup>2</sup>	0.6088	
	4	115	120	0.012	0.12	115	98761	162.390	1.9946	2.2106	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.1069	
											Std Err of Coef.	0.0606	
1C	1	115	12	0.012	0.12	11.5	889	106.110	-0.0511	2.0258	Constant	2.0779	120
	2	115	24	0.012	0.12	23	6272	167.280	0.7974	2.2234	Std Err of Y Est	0.0818	
	3	115	60	0.012	0.12	57.5	37691	198.090	1.5762	2.2969	r <sup>2</sup>	0.6692	
	4	115	120	0.012	0.12	115	98401	165.990	1.9930	2.2201	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.1053	
											Std Err of Coef.	0.0523	

Table D-2 (cont.) Day 30 results – K<sub>d</sub> experiments.

Soil	Sample		T	ungstate			X axis	Y axis	Log x axis	Log y axis	Regression Out	put	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed Wt. Sorbent (k					
2A	1	115	12	0.012	0.12	11.5	477	110.230	-0.3215	2.0423	Constant	2.1567	143
	2	115	24	0.012	0.12	23	2841	201.590	0.4535	2.3045	Std Err of Y Est	0.0854	1
	3	115	60	0.012	0.12	57.5	27084	304.160	1.4327	2.4831	r <sup>2</sup>	0.8802	
	4	115	120	0.012	0.12	115	86575	284.250	1.9374	2.4537	No. of Observations	4	1
				1		l	1		I.		Degrees of Freedom	2	1
											X Coefficient(s)	0.1875	1
											Std Err of Coef.	0.0489	1
2B	1	115	12	0.012	0.12	11.5	375	111.250	-0.4260	2.0463	Constant	2.1704	148
	2	115	24	0.012	0.12	23	2610	203.900	0.4166	2.3094	Std Err of Y Est	0.0852	1
	3	115	60	0.012	0.12	57.5	29326	281.740	1.4673	2.4498	r <sup>2</sup>	0.8558	1
	4	115	120	0.012	0.12	115	88835	261.650	1.9486	2.4177	No. of Observations	4	1
		•				ı	1	<u> </u>	•	•	Degrees of Freedom	2	1
											X Coefficient(s)	0.1591	1
											Std Err of Coef.	0.0462	1
2C	1	115	12	0.012	0.12	11.5	367	111.330	-0.4353	2.0466	Constant	2.1722	149
	2	115	24	0.012	0.12	23	2482	205.180	0.3948	2.3121	Std Err of Y Est	0.0645	1
	3	115	60	0.012	0.12	57.5	29363	281.370	1.4678	2.4493	r <sup>2</sup>	0.9298	
	4	115	120	0.012	0.12	115	84480	305.200	1.9268	2.4846	No. of Observations	4	1
		ı				1	ı	ı	ı	1	Degrees of Freedom	2	1
											X Coefficient(s)	0.1801	1
											Std Err of Coef.	0.035	

Table D-2 (cont.) Day 30 results – K<sub>d</sub> experiments.

Soil	Sample			Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	K <sub>d</sub>
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
ЗА	1	115	12	0.012	0.12	11.5	20	114.800	-1.6990	2.0599	Constant	2.4364	273
	2	115	24	0.012	0.12	23	898	221.020	-0.0467	2.3444	Std Err of Y Est	0.0671	
	3	115	60	0.012	0.12	57.5	8228	492.720	0.9153	2.6926	r <sup>2</sup>	0.9759	1
	4	115	120	0.012	0.12	115	44798	702.020	1.6513	2.8463	No. of Observations	4	1
		•	•		I.		1	1	•	•	Degrees of Freedom	2	1
											X Coefficient(s)	0.241	1
											Std Err of Coef.	0.0268	1
3B	1	115	12	0.012	0.12	11.5	22	114.780	-1.6576	2.0599	Constant	2.4359	273
	2	115	24	0.012	0.12	23	564	224.360	-0.2487	2.3509	Std Err of Y Est	0.0379	1
	3	115	60	0.012	0.12	57.5	8447	490.530	0.9267	2.6907	r <sup>2</sup>	0.9917	1
	4	115	120	0.012	0.12	115	50565	644.350	1.7039	2.8091	No. of Observations	4	1
			- <b>!</b>	<b>"</b>	I				l	I.	Degrees of Freedom	2	1
											X Coefficient(s)	0.2308	1
											Std Err of Coef.	0.0149	1
3C	1	115	12	0.012	0.12	11.5	53	114.470	-1.2757	2.0587	Constant	2.4203	263
	2	115	24	0.012	0.12	23	390	226.100	-0.4089	2.3543	Std Err of Y Est	0.036	1
	3	115	60	0.012	0.12	57.5	9837	476.630	0.9929	2.6782	r <sup>2</sup>	0.9929	1
	4	115	120	0.012	0.12	115	45433	695.670	1.6574	2.8424	No. of Observations	4	1
		· L	L .	1	1	1	-1	-1	L	L	Degrees of Freedom	2	1
											X Coefficient(s)	0.2612	1
											Std Err of Coef.	0.0156	1

Table D-2 (cont.) Day 30 results – K<sub>d</sub> experiments.

Soil	Sample			Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	K <sub>d</sub>
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
5A	1	115	12	0.012	0.12	11.5	250	112.500	-0.6021	2.0512	Constant	2.3983	250
	2	115	24	0.012	0.12	23	513	224.870	-0.2899	2.3519	Std Err of Y Est	0.1052	
	3	115	60	0.012	0.12	57.5	4101	533.990	0.6129	2.7275	r <sup>2</sup>	0.9532	
	4	115	120	0.012	0.12	115	26524	884.760	1.4236	2.9468	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.423	
											Std Err of Coef.	0.0663	
5B	1	115	12	0.012	0.12	11.5	210	112.900	-0.6778	2.0527	Constant	2.414	259
	2	115	24	0.012	0.12	23	478	225.220	-0.3206	2.3526	Std Err of Y Est	0.1126	1
	3	115	60	0.012	0.12	57.5	3707	537.930	0.5690	2.7307	r <sup>2</sup>	0.9449	1
	4	115	120	0.012	0.12	115	29493	855.070	1.4697	2.9320	No. of Observations	4	1
			1	1		•					Degrees of Freedom	2	1
											X Coefficient(s)	0.306	
											Std Err of Coef.	0.676	
5C	1	115	12	0.012	0.12	11.5	219	112.810	-0.6596	2.0523	Constant	2.4087	256
	2	115	24	0.012	0.12	23	471	225.290	-0.3270	2.3527	Std Err of Y Est	0.1191	1
	3	115	60	0.012	0.12	57.5	3826	536.740	0.5827	2.7298	r <sup>2</sup>	0.9374	
	4	115	120	0.012	0.12	115	31180	838.200	1.4939	2.9233	No. of Observations	4	1
		•	•	•	•	ı	•	1	•		Degrees of Freedom	2	1
											X Coefficient(s)	0.3884	1
											Std Err of Coef.	0.071	1

Table D-2 (cont.) Day 30 results – K<sub>d</sub> experiments.

Soil	Sample			Tungstate	)		X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	K <sub>d</sub>
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
6A	1	115	12	0.012	0.12	11.5	80	114.200	-1.0969	2.0577	Constant	2.5236	334
	2	115	24	0.012	0.12	23	158	228.420	-0.8013	2.3587	Std Err of Y Est	0.1149	
	3	115	60	0.012	0.12	57.5	2996	545.040	0.4765	2.7364	r <sup>2</sup>	0.9434	1
	4	115	120	0.012	0.12	115	26992	880.080	1.4312	2.9445	No. of Observations	4	]
		1		1	•	ı	1	1	•		Degrees of Freedom	2	]
											X Coefficient(s)	0.3269	]
											Std Err of Coef.	0.0566	]
6B	1	115	12	0.012	0.12	11.5	105	113.950	-0.9788	2.0567	Constant	2.4977	315
	2	115	24	0.012	0.12	23	200	228.000	-0.6990	2.3579	Std Err of Y Est	0.1201	
	3	115	60	0.012	0.12	57.5	3187	543.130	0.5034	2.7349	r <sup>2</sup>	0.9374	]
	4	115	120	0.012	0.12	115	28635	863.650	1.4569	2.9363	No. of Observations	4	]
		1	·!	1		ı	1	1	•		Degrees of Freedom	2	]
											X Coefficient(s)	0.3369	]
											Std Err of Coef.	0.0616	]
6C	1	115	12	0.012	0.12	11.5	42	114.580	-1.3768	2.0591	Constant	2.533	341
	2	115	24	0.012	0.12	23	155	228.450	-0.8097	2.3588	Std Err of Y Est	0.0857	]
	3	115	60	0.012	0.12	57.5	3132	543.680	0.4958	2.7353	r <sup>2</sup>	0.9671	
	4	115	120	0.012	0.12	115	31441	835.590	1.4975	2.9220	No. of Observations	4	1
		•				1	•	•		1	Degrees of Freedom	2	1
											X Coefficient(s)	0.293	1
											Std Err of Coef.	0.0382	]

Table D-3. Day 60 results − K<sub>d</sub> experiments.

Soil	Sample			Tungstate	•		X axis	Y axis	Log x axis	Log y axis	Regression Ou	ıtput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
1A	1	115	12	0.01	0.12	11.5	1228	102.720	0.0892	2.0117	Constant	2.0616	115
	2	115	24	0.012	0.12	23	5076	179.240	0.7055	2.2534	Std Err of Y Est	0.082	
	3	115	60	0.012	0.12	57.5	38512	189.880	1.5856	2.2785	r <sup>2</sup>	0.758	1
	4	115	120	0.012	0.12	115	94647	203.530	1.9761	2.3086	No. of Observations	4	]
		•	l	1	1	l					Degrees of Freedom	2	1
											X Coefficient(s)	0.139	
											Std Err of Coef.	0.0556	
1B	1	115	12	0.012	0.12	11.5	1476	100.240	0.1691	2.0010	Constant	2.1069	128
	2	115	24	0.012	0.12	23	5729	172.710	0.7581	2.2373	Std Err of Y Est	0.173	
	3	115	60	0.012	0.12	57.5	39173	183.270	1.5930	2.2631	r <sup>2</sup>	0.0113	
	4	115	120	0.012	0.12	115	104799	102.010	2.0204	2.0086	No. of Observations	4	]
			I								Degrees of Freedom	2	-
											X Coefficient(s)	0.0182	1
											Std Err of Coef.	0.0113	
1C	1	115	12	0.012	0.12	11.5					Constant		119
	2	115	24	0.012	0.12	23					Std Err of Y Est		
	3	115	60	0.012	0.12	57.5					r <sup>2</sup>		
	4	115	120	0.012	0.12	115					No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)		]
											Std Err of Coef.		

Soil	Sample			Tungstat	е		X axis	Y axis	Log x axis	Log y axis	Regression Ou	ıtput	K <sub>d</sub>
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
2A	1	115	12	0.012	0.12	11.5	918	105.820	-0.0372	2.0246	Constant	2.0801	120
	2	115	24	0.012	0.12	23	3695	193.050	0.5676	2.2857	Std Err of Y Est	0.0608	1
	3	115	60	0.012	0.12	57.5	27464	300.360	1.4388	2.4776	r <sup>2</sup>	0.954	
	4	115	120	0.012	0.12	115	80445	345.550	1.9055	2.5385	No. of Observations	4	1
											Degrees of Freedom	2	
											X Coefficient(s)	0.2597	1
											Std Err of Coef.	0.0403	1
2B	1	115	12	0.012	0.12	11.5	470	110.300	-0.3279	2.0426	Constant	2.163	146
	2	115	24	0.012	0.12	23	2770	202.300	0.4425	2.3060	Std Err of Y Est	0.1044	1
	3	115	60	0.012	0.12	57.5	25754	317.460	1.4108	2.5017	r <sup>2</sup>	0.8218	1
	4	115	120	0.012	0.12	115	88063	269.370	1.9448	2.4303	No. of Observations	4	
			1	1	1	<u>,</u>	•	•			Degrees of Freedom	2	
											X Coefficient(s)	0.1811	
											Std Err of Coef.	0.0596	
2C	1	115	12	0.012	0.12	11.5	394	111.060	-0.4045	2.0456	Constant	2.1704	148
	2	115	24	0.012	0.12	23	2572	204.280	0.4103	2.3102	Std Err of Y Est	0.0768	1
	3	115	60	0.012	0.12	57.5	27674	298.260	1.4421	2.4746	r <sup>2</sup>	0.9021	
	4	115	120	0.012	0.12	115	85772	292.280	1.9333	2.4658	No. of Observa- tions	4	
											Degrees of Free- dom	2	
											X Coefficient(s)	0.1817	_
											Std Err of Coef.	0.0423	

Soil	Sample			Tungstate			X axis	Y axis	Log x axis	Log y axis		Regression Out	put	K <sub>d</sub>
	,	Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)						
4A	1	115	12	0.012	0.12	11.5	2126	93.740	0.3276	1.9719	Consta	ant	2.0636	116
	2	115	24	0.012	0.12	23	7548	154.520	0.8778	2.1890	Std Err	of Y Est	0.1259	
	3	115	60	0.012	0.12	57.5	44390	131.100	1.6473	2.1176	r <sup>2</sup>		0.0008	
	4	115	120	0.012	0.12	115	105124	98.760	2.0217	1.9946	No. of	Observations	4	
											Degree	s of Freedom	2	
											X Coef	ficient(s)	0.0038	
											Std Err	of Coef.	0.0955	
4B	1	115	12	0.012	0.12	11.5	1632	98.680	0.2127	1.9942	Consta	ant	2.0346	108
	2	115	24	0.012	0.12	23	8059	149.410	0.9063	2.1744	Std Err	of Y Est	0.0761	
	3	115	60	0.012	0.12	57.5	43551	139.490	1.6390	2.1445	r <sup>2</sup>		0.3835	
	4	115	120	0.012	0.12	115	101868	131.320	2.0080	2.1183	No. of	Observations	4	
											Degree	es of Freedom	2	
											X Coef	ficient(s)	0.0615	
												of Coef.	0.0551	
4C	1	115	12	0.012	0.12	11.5	1661	98.390	0.2204		1.99 30	Constant	2.0741	119
	2	115	24	0.012	0.12	23	7822	151.780	0.8933		2.18 12	Std Err of Y Est	0.132	
	3	115	60	0.012	0.12	57.5	42861	146.390	1.6321		2.16 55	r <sup>2</sup>	0.0014	
	4	115	120	0.012	0.12	115	105425	95.750	2.0229		1.98 11	No. of Observations	4	
											Degree	es of Freedom	2	
											X Coef	ficient(s)	0.0051	
											Std Err	of Coef.	0.0953	

Table D-3 (cont.) Day 60 results –  $K_d$  experiments.

Soil	Sample			Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)		Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
5A	1	115	12	0.012	0.12	11.5	246	112.540	-0.6091	2.0513	Constant	2.5095	323
	2	115	24	0.012	0.12	23	320	226.800	-0.4949	2.3556	Std Err of Y Est	0.1276	
	3	115	60	0.012	0.12	57.5	2214	552.860	0.3452	2.7426	r <sup>2</sup>	0.9402	1
	4	115	120	0.012	0.12	115	10046	1049.540	1.0020	3.0210	No. of Observations	4	
		1	•	•	•		•	1			Degrees of Freedom	2	1
											X Coefficient(s)	0.5453	1
											Std Err of Coef.	0.0972	1
5B	1	115	12	0.012	0.12	11.5	165	113.350	-0.7825	2.0544	Constant	2.5293	338
	2	115	24	0.012	0.12	23	335	226.650	-0.4750	2.3554	Std Err of Y Est	0.1119	1
	3	115	60	0.012	0.12	57.5	1765	557.350	0.2467	2.7461	r <sup>2</sup>	0.953	1
	4	115	120	0.012	0.12	115	12851	1021.490	1.1089	3.0092	No. of Observations	4	1
		II.	1						l		Degrees of Freedom	2	1
											X Coefficient(s)	0.4886	
											Std Err of Coef.	0.0767	1
5C	1	115	12	0.012	0.12	11.5	144	113.560	-0.8416	2.0552	Constant	2.5512	356
	2	115	24	0.012	0.12	23	293	227.070	-0.5331	2.3562	Std Err of Y Est	0.1036	1
	3	115	60	0.012	0.12	57.5	1721	557.790	0.2358	2.7465	r <sup>2</sup>	0.9599	1
	4	115	120	0.012	0.12	115	11759	1032.410	1.0704	3.0139	No. of Observations	4	1
		1	1	1	1	1	_1	<u> </u>	<u> </u>	1	Degrees of Freedom	2	1
											X Coefficient(s)	0.4844	1
											Std Err of Coef.	0.07	1

Table D-3 (cont.) Day 60 results – K<sub>d</sub> experiments.

Soil	Sample			Tungstat	е		X axis	Y axis	Log x axis	Log y axis	Regression Out	tput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
6A	1	115	12	0.012	0.12	11.5	128	113.720	-0.8928	2.0558	Constant	2.4771	300
	2	115	24	0.012	0.12	23	260	227.400	-0.5850	2.3568	Std Err of Y Est	0.1002	
	3	115	60	0.012	0.12	57.5	3916	535.840	0.5928	2.7290	r <sup>2</sup>	0.9577	
	4	115	120	0.012	0.12	115	24922	900.780	1.3966	2.9546	No. of Observations	4	
		•	•		•		1				Degrees of Freedom	2	
											X Coefficient(s)	0.3669	
											Std Err of Coef.	0.0545	
6B	1	115	12	0.012	0.12	11.5	112	113.880	-0.9508	2.0564	Constant	2.4664	293
	2	115	24	0.012	0.12	23	394	226.060	-0.4045	2.3542	Std Err of Y Est	0.0736	
	3	115	60	0.012	0.12	57.5	3479	540.210	0.5415	2.7326	r <sup>2</sup>	0.977	
	4	115	120	0.012	0.12	115	26159	888.410	1.4176	2.9486	No. of Observations	4	
		•	•		•		1				Degrees of Freedom	2	
											X Coefficient(s)	0.3747	
											Std Err of Coef.	0.0406	
6C	1	115	12	0.012	0.12	11.5	105	113.950	-0.9788	2.0567	Constant	2.4498	282
	2	115	24	0.012	0.12	23	253	227.470	-0.5969	2.3569	Std Err of Y Est	0.0918	
	3	115	60	0.012	0.12	57.5	7382	501.180	0.8682	2.7000	r <sup>2</sup>	0.9619	
	4	115	120	0.012	0.12	115	29506	854.940	1.4699	2.9319	No. of Observations	4	
					•		1				Degrees of Freedom	2	
											X Coefficient(s)	0.3231	1
											Std Err of Coef.	0.0454	

Soil	Sample			Tungstate	•		X axis	Y axis	Log x axis	Log y axis	Regression Ou	ıtput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
1A	1	115	12	0.01	0.12	11.5	1231	102.690	0.0903	2.0115	Constant	2.0294	107
	2	115	24	0.012	0.12	23	5152	178.480	0.7120	2.2516	Std Err of Y Est	0.0716	
	3	115	60	0.012	0.12	57.5	37381	201.190	1.5727	2.3036	r <sup>2</sup>	0.9002	
	4	115	120	0.012	0.12	115	86309	286.910	1.9361	2.4577	No. of Observations	4	
					I		l	l			Degrees of Freedom	2	
											X Coefficient(s)	0.2104	
											Std Err of Coef.	0.0495	
1B	1	115	12	0.012	0.12	11.5	1246	102.540	0.0955	2.0109	Constant	2.0348	108
	2	115	24	0.012	0.12	23	5856	171.440	0.7676	2.2341	Std Err of Y Est	0.0564	
	3	115	60	0.012	0.12	57.5	37556	199.440	1.5747	2.2998	r <sup>2</sup>	0.9083	
	4	115	120	0.012	0.12	115	92158	228.420	1.9645	2.3587	No. of Observations	4	
		1		ı							Degrees of Freedom	2	=
											X Coefficient(s)	0.1736	
											Std Err of Coef.	0.039	
1C	1	115	12	0.012	0.12	11.5	1232	102.680	0.0906	2.0115	Constant	2.0174	104
	2	115	24	0.012	0.12	23	6511	164.890	0.8136	2.2172	Std Err of Y Est	0.0346	
	3	115	60	0.012	0.12	57.5	35766	217.340	1.5535	2.3371	r <sup>2</sup>	0.9717	
	4	115	120	0.012	0.12	115	90474	245.260	1.9565	2.3896	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.2007	
											Std Err of Coef.	0.0242	

Table D-4 (cont.) Day 90 results – K<sub>d</sub> experiments.

Soil	Sample	le Tungstate				X axis	Y axis	Log x axis	Log y axis	Regression Output		K <sub>d</sub>	
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
2A	1	115	12	0.012	0.12	11.5	933	105.670	-0.0301	2.0240	Constant	2.0619	115
	2	115	24	0.012	0.12	23	4115	188.850	0.6144	2.2761	Std Err of Y Est	0.0427	
	3	115	60	0.012	0.12	57.5	25847	316.530	1.4124	2.5004	r <sup>2</sup>	0.9807	
	4	115	120	0.012	0.12	115	76768	382.320	1.8852	2.5824	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.2924	
											Std Err of Coef.	0.029	
2B	1	115	12	0.012	0.12	11.5	475	110.250	-0.3233	2.0424	Constant	2.1685	147
	2	115	24	0.012	0.12	23	2349	206.510	0.3709	2.3149	Std Err of Y Est	0.0834	
	3	115	60	0.012	0.12	57.5	25234	322.660	1.4020	2.5087	r <sup>2</sup>	0.905	
	4	115	120	0.012	0.12	115	82645	323.550	1.9172	2.5099	No. of Observations	4	
			•	•							Degrees of Freedom	2	
											X Coefficient(s)	0.0285	
											Std Err of Coef.	0.0478	
2C	1	115	12	0.012	0.12	11.5	743	107.570	-0.1290	2.0317	Constant	2.1301	135
	2	115	24	0.012	0.12	23	3426	195.740	0.5348	2.2917	Std Err of Y Est	0.132	
	3	115	60	0.012	0.12	57.5	26068	314.320	1.4161	2.4974	r <sup>2</sup>	0.7002	
	4	115	120	0.012	0.12	115	91443	235.570	1.9612	2.3721	No. of Observa- tions	4	
											Degrees of Freedom		
											X Coefficient(s)	0.1777	
	1										Std Err of Coef.	0.0822	

Table D-4 (cont.) Day 90 results – K<sub>d</sub> experiments.

Soil	Sample		T	ungstate			X axis	Y axis	Log x axis	Log y axis	Regression Output		K <sub>d</sub>
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
ЗА	1	115	12	0.012	0.12	11.5	180	113.200	-0.7447	2.0538	Constant	2.3303	214
	2	115	24	0.012	0.12	23	1092	219.080	0.0382	2.3406	Std Err of Y Est	0.0227	1
	3	115	60	0.012	0.12	57.5	8317	491.830	0.9200	2.6918	r <sup>2</sup>	0.9975	
	4	115	120	0.012	0.12	115	37786	772.140	1.5773	2.8877	No. of Observations	4	
			'	•		•					Degrees of Freedom	2	
											X Coefficient(s)	0.3645	
											Std Err of Coef.	0.0129	
3B	1	115	12	0.012	0.12	11.5	122	113.780	-0.9136	2.0561	Constant	2.3617	230
	2	115	24	0.012	0.12	23	874	221.260	-0.0585	2.3449	Std Err of Y Est	0.0221	
	3	115	60	0.012	0.12	57.5	8570	489.300	0.9330	2.6896	r <sup>2</sup>	0.9975	
	4	115	120	0.012	0.12	115	41056	739.440	1.6134	2.8689	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.3257	
											Std Err of Coef.	0.0115	
3C	1	115	12	0.012	0.12	11.5	306	111.940	-0.5143	2.0490	Constant	2.3265	212
	2	115	24	0.012	0.12	23	586	224.140	-0.2321	2.3505	Std Err of Y Est	0.1187	
	3	115	60	0.012	0.12	57.5	8401	490.990	0.9243	2.6911	r <sup>2</sup>	0.9233	
	4	115	120	0.012	0.12	115	47861	671.390	1.6800	2.8270	No. of Observations	4	1
		•	1		1	ı	•		•		Degrees of Freedom	2	1
											X Coefficient(s)	0.3291	1
											Std Err of Coef.	0.0671	

Soil	Sample		•	Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression Output		Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
4A	1	115	12	0.012	0.12	11.5	1669	98.310	0.2225	1.9926	Constant	2.1293	135
	2	115	24	0.012	0.12	23	7084	159.160	0.8503	2.2018	Std Err of Y Est	0.1862	
	3	115	60	0.012	0.12	57.5	44473	130.270	1.6481	2.1148	r <sup>2</sup>	0.1598	
	4	115	120	0.012	0.12	115	108405	65.950	2.0350	1.8192	No. of Observations	4	
		•	•		•						Degrees of Freedom	2	
											X Coefficient(s)	-0.082	
											Std Err of Coef.	0.1325	
4B	1	115	12	0.012	0.12	11.5	1424	100.760	0.1535	2.0033	Constant	2.0673	117
	2	115	24	0.012	0.12	23	7426	155.740	0.8708	2.1924	Std Err of Y Est	0.1066	
	3	115	60	0.012	0.12	57.5	42478	150.220	1.6282	2.1767	r <sup>2</sup>	0.0982	
	4	115	120	0.012	0.12	115	103547	114.530	2.0151	2.0589	No. of Observations	4	
		•	•		•						Degrees of Freedom	2	
											X Coefficient(s)	0.0348	
											Std Err of Coef.	0.0745	
4C	1	115	12	0.012	0.12	11.5	1772	97.280	0.2485	1.9880	Constant	2.126	134
	2	115	24	0.012	0.12	23	7216	157.840	0.8583	2.1982	Std Err of Y Est	0.2061	
	3	115	60	0.012	0.12	57.5	42451	150.490	1.6279	2.1775	r <sup>2</sup>	0.0898	
	4	115	120	0.012	0.12	115	108339	66.610	2.0348	1.8235	No. of Observations	4	
		ı	ı	1	ı	1		1	•		Degrees of Freedom	2	
											X Coefficient(s)	-0.066	1
											Std Err of Coef.	0.1494	

Table D-4 (cont.) Day 90 results – K<sub>d</sub> experiments.

Soil	Sample		T	ungstate			X axis	Y axis	Log x axis	Log y axis	Regression Output		Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
5A	1	115	12	0.012	0.12	11.5	274	112.260	-0.5622	2.0502	Constant	2.5166	329
	2	115	24	0.012	0.12	23	300	227.000	-0.5229	2.3560	Std Err of Y Est	0.1444	
	3	115	60	0.012	0.12	57.5	2197	553.030	0.3418	2.7427	r <sup>2</sup>	0.9245	
	4	115	120	0.012	0.12	115	8614	1063.860	0.9352	3.0269	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.5672	
											Std Err of Coef.	0.1151	
5B	1	115	12	0.012	0.12	11.5	198	113.020	-0.7033	2.0532	Constant	2.5028	318
	2	115	24	0.012	0.12	23	459	225.410	-0.3382	2.3530	Std Err of Y Est	0.076	
	3	115	60	0.012	0.12	57.5	2055	554.450	0.3128	2.7439	r <sup>2</sup>	0.9787	
	4	115	120	0.012	0.12	115	10319	1046.810	1.0136	3.0199	No. of Observations	4	
				•	•						Degrees of Freedom	2	
											X Coefficient(s)	0.5572	
											Std Err of Coef.	0.0581	
5C	1	115	12	0.012	0.12	11.5	153	113.470	-0.8153	2.0549	Constant	2.5549	359
	2	115	24	0.012	0.12	23	278	227.220	-0.5560	2.3564	Std Err of Y Est	0.0945	
	3	115	60	0.012	0.12	57.5	1950	555.500	0.2900	2.7447	r <sup>2</sup>	0.9671	
	4	115	120	0.012	0.12	115	9953	1050.470	0.9980	3.0214	No. of Observations	4	
		•	1		1	ı	•	•			Degrees of Freedom	2	1
											X Coefficient(s)	0.5057	1
											Std Err of Coef.	0.0659	

Table D-4 (cont.) Day 90 results – K<sub>d</sub> experiments.

Soil	Sample			Tungstate	<u> </u>		X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
6A	1	115	12	0.012	0.12	11.5	108	113.920	-0.9666	2.0566	Constant	2.4952	313
	2	115	24	0.012	0.12	23	245	227.550	-0.6108	2.3571	Std Err of Y Est	0.0993	1
	3	115	60	0.012	0.12	57.5	3277	542.230	0.5155	2.7342	r <sup>2</sup>	0.9586	
	4	115	120	0.012	0.12	115	25001	899.990	1.3980	2.9542	No. of Observations	4	]
			•								Degrees of Freedom	2	
											X Coefficient(s)	0.361	
											Std Err of Coef.	0.0531	
6B	1	115	12	0.012	0.12	11.5	144	113.560	-0.8416	2.0552	Constant	2.4729	297
	2	115	24	0.012	0.12	23	313	226.870	-0.5045	2.3558	Std Err of Y Est	0.0928	]
	3	115	60	0.012	0.12	57.5	3549	539.510	0.5501	2.7320	r <sup>2</sup>	0.9646	
	4	115	120	0.012	0.12	115	22307	926.930	1.3484	2.9670	No. of Observations	4	
					•						Degrees of Freedom	2	
											X Coefficient(s)	0.3955	1
											Std Err of Coef.	0.0535	1
6C	1	115	12	0.012	0.12	11.5	82	114.180	-1.0862	2.0576	Constant	2.484	305
	2	115	24	0.012	0.12	23	223	227.770	-0.6517	2.3575	Std Err of Y Est	0.0798	1
	3	115	60	0.012	0.12	57.5	5602	518.980	0.7483	2.7152	r <sup>2</sup>	0.9724	
	4	115	120	0.012	0.12	115	26363	886.370	1.4210	2.9476	No. of Observations	4	
		•	•	•	•	•	•	•	•	•	Degrees of Freedom	2	
											X Coefficient(s)	0.3292	
											Std Err of Coef.	0.0392	

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Soil	Sample			Tungsta	te		X axis	Y axis	Log x axis	Log y axis	Regression Ou	ıtput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
1A	1	115	12	0.01	0.12	11.5	1417	100.830	0.1514	2.0036	Constant	1.9621	92
	2	115	24	0.012	0.12	23	6317	166.830	0.8005	2.2223	Std Err of Y Est	0.0155	
	3	115	60	0.012	0.12	57.5	31800	257.000	1.5024	2.4099	r <sup>2</sup>	0.9972	
	4	115	120	0.012	0.12	115	79222	357.780	1.8988	2.5536	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.3081	
											Std Err of Coef.	0.0116	
1B	1	115	12	0.012	0.12	11.5	1292	102.080	0.1113	2.0089	Constant	1.9858	97
	2	115	24	0.012	0.12	23	5972	170.280	0.7761	2.2312	Std Err of Y Est	0.0403	
	3	115	60	0.012	0.12	57.5	33908	235.920	1.5303	2.3728	r <sup>2</sup>	0.9789	
	4	115	120	0.012	0.12	115	79953	350.470	1.9028	2.5447	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.281	
											Std Err of Coef.	0.0291	
1C	1	115	12	0.012	0.12	11.5	1368	101.320	0.1361	2.0057	Constant	1.9706	93
	2	115	24	0.012	0.12	23	5904	170.960	0.7711	2.2329	Std Err of Y Est	0.0126	
	3	115	60	0.012	0.12	57.5	29953	275.470	1.4764	2.4401	r <sup>2</sup>	0.9983	
	4	115	120	0.012	0.12	115	77460	375.400	1.8891	2.5745	No. of Observations	4	
		_									Degrees of Freedom	2	
											X Coefficient(s)	0.3209	
											Std Err of Coef.	0.0094	

Table D-5 (cont.) Day 120 results - K<sub>d</sub> experiments.

Soil	Sample			Tungstate	•		X axis	Y axis	Log x axis	Log y axis	Regression Out	put	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)		Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
2A	1	115	12	0.012	0.12	11.5	458	110.420	-0.3391	2.0430	Constant	2.1754	150
	2	115	24	0.012	0.12	23	1897	211.030	0.2781	2.3243	Std Err of Y Est	0.0766	1
	3	115	60	0.012	0.12	57.5	26697	308.030	1.4265	2.4886	r <sup>2</sup>	0.9455	1
	4	115	120	0.012	0.12	115	67617	473.830	1.8301	2.6756	No. of Observations	4	1
		•		W.		.1	1	1	1	1	Degrees of Freedom	2	1
											X Coefficient(s)	0.2598	1
											Std Err of Coef.	0.0441	1
2B	1	115	12	0.012	0.12	11.5	278	112.220	-0.5560	2.0501	Constant	2.2179	165
	2	115	24	0.012	0.12	23	1605	213.950	0.2055	2.3303	Std Err of Y Est	0.0567	1
	3	115	60	0.012	0.12	57.5	24810	326.900	1.3946	2.5144	r <sup>2</sup>	0.9675	
	4	115	120	0.012	0.12	115	71143	438.570	1.8521	2.6420	No. of Observations	4	1
		•		W.		.1	1	1	1	1	Degrees of Freedom	2	1
											X Coefficient(s)	0.2297	1
											Std Err of Coef.	0.0298	1
2C	1	115	12	0.012	0.12	11.5	232	112.680	-0.6345	2.0518	Constant	2.2288	169
	2	115	24	0.012	0.12	23	1491	215.090	0.1735	2.3326	Std Err of Y Est	0.0575	1
	3	115	60	0.012	0.12	57.5	25180	323.200	1.4011	2.5095	r <sup>2</sup>	0.9639	
	4	115	120	0.012	0.12	115	73548	414.520	1.8666	2.6175	No. of Observations	4	
				1	L	ı	1	ı			Degrees of Freedom	2	
											X Coefficient(s)	0.2124	
	1										Std Err of Coef.	0.0291	

## Table D-5 (cont.) Day 120 results – K<sub>d</sub> experiments.

Soil	Sample		•	Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	after	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
3A	1	115	12	0.012	0.12	11.5	51	114.490	-1.2924	2.0588	Constant	2.4102	257
	2	115	24	0.012	0.12	23	951	220.490	-0.0218	2.3434	Std Err of Y Est	0.0502	1
-	3	115	60	0.012	0.12	57.5	8182	493.180	0.9129	2.6930	r <sup>2</sup>	0.9877	
	4	115	120	0.012	0.12	115	37161	778.390	1.5701	2.8912	No. of Observations	4	1
		ı	I.		ı		1				Degrees of Freedom	2	
											X Coefficient(s)	0.2956	
											Std Err of Coef.	0.0233	
3B	1	115	12	0.012	0.12	11.5	70	114.300	-1.1549	2.0580	Constant	2.4096	257
50	2	115	24	0.012	0.12	23	561	224.390	-0.2510	2.3510	Std Err of Y Est	0.0149	
	3	115	60	0.012	0.12	57.5	8622	488.780	0.9356	2.6891	r <sup>2</sup>	0.9989	
	4	115	120	0.012	0.12	115	40169	748.310	1.6039	2.8741	No. of Observations	4	
			•	•			1	1			Degrees of Freedom	2	
											X Coefficient(s)	0.2946	
											Std Err of Coef.	0.007	
3C	1	115	12	0.012	0.12	11.5	89	114.110	-1.0506	2.0573	Constant	2.3961	249
-	2	115	24	0.012	0.12	23	517	224.830	-0.2865	2.3519	Std Err of Y Est	0.0583	
-	3	115	60	0.012	0.12	57.5	7858	496.420	0.8953	2.6958	r <sup>2</sup>	0.9814	
	4	115	120	0.012	0.12	115	47320	676.800	1.6750	2.8305	No. of Observations	4	
		•	•	•	•		•	•			Degrees of Freedom	2	
											X Coefficient(s)	0.2847	
											Std Err of Coef.	0.0277	

Soil	Sample			Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	K <sub>d</sub>
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	after	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
4A	1	115	12	0.012	0.12	11.5	1345	101.550	0.1287	2.0067	Constant	2.0558	114
	2	115	24	0.012	0.12	23	4489	185.110	0.6521	2.2674	Std Err of Y Est	0.0891	
	3	115	60	0.012	0.12	57.5	36830	206.700	1.5662	2.3153	r <sup>2</sup>	0.7921	
	4	115	120	0.012	0.12	115	91859	231.410	1.9631	2.3644	No. of Observations	4	
		Ш	JI.	JI.	ı	ı	•	•	•	•	Degrees of Freedom	2	
											X Coefficient(s)	0.1695	
											Std Err of Coef.	0.0614	
4B	1	115	12	0.012	0.12	11.5	851	106.490	-0.0701	2.0273	Constant	2.0556	114
	2	115	24	0.012	0.12	23	5289	177.110	0.7234	2.2482	Std Err of Y Est	0.0544	
	3	115	60	0.012	0.12	57.5	36210	212.900	1.5588	2.3282	r <sup>2</sup>	0.9472	
	4	115	120	0.012	0.12	115	83904	310.960	1.9238	2.4927	No. of Observations	4	
		Ш	JI.	JI.	ı	ı	•	•	•	•	Degrees of Freedom	2	
											X Coefficient(s)	0.2113	
											Std Err of Coef.	0.0353	
4C	1	115	12	0.012	0.12	11.5	1440	100.600	0.1584	2.0026	Constant	2.0085	102
	2	115	24	0.012	0.12	23	6476	165.240	0.8113	2.2181	Std Err of Y Est	0.0562	
	3	115	60	0.012	0.12	57.5	35186	223.140	1.5464	2.3486	r <sup>2</sup>	0.9236	
	4	115	120	0.012	0.12	115	92097	229.030	1.9642	2.3599	No. of Observations	4	
		1		•							Degrees of Freedom	2	
											X Coefficient(s)	0.1198	
											Std Err of Coef.	0.0406	

Soil	Sample	ample Tungstate			X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	Kd		
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
5A	1	115	12	0.012	0.12	11.5	94	114.060	-1.0269	2.0571	Constant	2.6485	445
	2	115	24	0.012	0.12	23	255	227.450	-0.5935	2.3569	Std Err of Y Est	0.0582	
	3	115	60	0.012	0.12	57.5	1230	562.700	0.0899	2.7503	r <sup>2</sup>	0.9878	
	4	115	120	0.012	0.12	115	6258	1087.420	0.7964	3.0364	No. of Observations	4	
		•	•	•	•		•	1			Degrees of Freedom	2	
											X Coefficient(s)	0.5361	
											Std Err of Coef.	0.0468	
5B	1	115	12	0.012	0.12	11.5	82	114.180	-1.0862	2.0576	Constant	2.6615	459
	2	115	24	0.012	0.12	23	194	228.060	-0.7122	2.3580	Std Err of Y Est	0.0689	
	3	115	60	0.012	0.12	57.5	1239	562.610	0.0931	2.7502	r <sup>2</sup>	0.9829	
	4	115	120	0.012	0.12	115	6578	1084.220	0.8181	3.0351	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.5015	
											Std Err of Coef.	0.0468	
5C	1	115	12	0.012	0.12	11.5	90	114.100	-1.0458	2.0573	Constant	2.6685	466
	2	115	24	0.012	0.12	23	164	228.360	-0.7852	2.3586	Std Err of Y Est	0.1063	
	3	115	60	0.012	0.12	57.5	1063	564.370	0.0265	2.7516	r <sup>2</sup>	0.9592	
	4	115	120	0.012	0.12	115	6975	1080.250	0.8435	3.0335	No. of Observations	4	
		1						1	1		Degrees of Freedom	2	
											X Coefficient(s)	0.4923	
											Std Err of Coef.	0.0718	

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Soil	Sample			Tungstat	е		X axis	Y axis	Log x axis	Log y axis	Regression Out	tput	K <sub>d</sub>
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
6A	1	115	12	0.012	0.12	11.5	36	114.640	-1.4437	2.0593	Constant	2.5985	397
	2	115	24	0.012	0.12	23	198	228.020	-0.7033	2.3580	Std Err of Y Est	0.0423	
	3	115	60	0.012	0.12	57.5	1934	555.660	0.2865	2.7448	r <sup>2</sup>	0.993	
	4	115	120	0.012	0.12	115	15882	991.180	1.2009	2.9962	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.3575	
											Std Err of Coef.	0.0212	
6B	1	115	12	0.012	0.12	11.5	36	114.640	-1.4437	2.0593	Constant	2.5777	378
	2	115	24	0.012	0.12	23	198	228.020	-0.7033	2.3580	Std Err of Y Est	0.0927	
	3	115	60	0.012	0.12	57.5	1934	555.660	0.2865	2.7448	r <sup>2</sup>	0.9658	
	4	115	120	0.012	0.12	115	15882	991.180	1.2009	2.9962	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.36	
											Std Err of Coef.	0.0479	
6C	1	115	12	0.012	0.12	11.5	32	114.680	-1.4949	2.0595	Constant	2.603	401
	2	115	24	0.012	0.12	23	127	228.730	-0.8962	2.3593	Std Err of Y Est	0.0779	
	3	115	60	0.012	0.12	57.5	1768	557.320	0.2475	2.7461	r <sup>2</sup>	0.9756	
	4	115	120	0.012	0.12	115	20263	947.370	1.3067	2.9765	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.3234	
											Std Err of Coef.	0.0362	

Table D-6. Day 180 results –  $K_{\text{\scriptsize d}}$  experiments.

Soil	Sample			Tungstat	te		X axis	Y axis	Log x axis	Log y axis	Regression Ou	ıtput	K <sub>d</sub>
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
1A	1	115	12	0.01	0.12	11.5	1879	96.210	0.2739	1.9832	Constant	1.8864	77
	2	115	24	0.012	0.12	23	5613	173.870	0.7492	2.2402	Std Err of Y Est	0.0379	
	3	115	60	0.012	0.12	57.5	28184	293.160	1.4500	2.4671	r <sup>2</sup>	0.9891	-
	4	115	120	0.012	0.12	115	68074	469.260	1.8330	2.6714	No. of Observations	4	-
			•	•			•				Degrees of Freedom	2	
											X Coefficient(s)	0.422	
											Std Err of Coef.	0.031	
1B	1	115	12	0.012	0.12	11.5	1483	100.170	0.1711	2.0007	Constant	1.9597	91
	2	115	24	0.012	0.12	23	5450	175.500	0.7364	2.2443	Std Err of Y Est	0.0262	
	3	115	60	0.012	0.12	57.5	27450	300.500	1.4385	2.4778	r <sup>2</sup>	0.9935	
	4	115	120	0.012	0.12	115	74793	402.070	1.8739	2.6043	No. of Observations	4	
			•				•				Degrees of Freedom	2	•
											X Coefficient(s)	0.353	
											Std Err of Coef.	0.02	
1C	1	115	12	0.012	0.12	11.5	1411	100.890	0.1495	2.0038	Constant	2.0404	110
	2	115	24	0.012	0.12	23	5868	171.320	0.7685	2.2338	Std Err of Y Est	0.1427	
	3	115	60	0.012	0.12	57.5	27259	302.410	1.4355	2.4806	r <sup>2</sup>	0.6592	
	4	115	120	0.012	0.12	115	93729	212.710	1.9719	2.3278	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)		
											Std Err of Coef.		

## Table D-6 (cont.) Day 180 results – K<sub>d</sub> experiments.

Soil	Sample			Tungsta	te		X axis	Y axis	Log x axis	Log y axis	Regression Out	put	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
2A	1	115	12	0.012	0.12	11.5	510	109.900	-0.2924	2.0410	Constant	2.187	154
	2	115	24	0.012	0.12	23	1801	211.990	0.2555	2.3263	Std Err of Y Est	0.1132	]
	3	115	60	0.012	0.12	57.5	21848	356.520	1.3394	2.5521	r <sup>2</sup>	0.846	]
	4	115	120	0.012	0.12	115	81663	333.370	1.9120	2.5229	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.216	
											Std Err of Coef.	0.0652	
2B	1	115	12	0.012	0.12	11.5	189	113.110	-0.7235	2.0535	Constant	2.232	171
	2	115	24	0.012	0.12	23	1348	216.520	0.1297	2.3355	Std Err of Y Est	0.0694	]
	3	115	60	0.012	0.12	57.5	28325	291.750	1.4522	2.4650	r <sup>2</sup>	0.9344	
	4	115	120	0.012	0.12	115	78416	365.840	1.8944	2.5633	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.1777	
											Std Err of Coef.	0.0333	
2C	1	115	12	0.012	0.12	11.5	162	113.380	-0.7905	2.0545	Constant	2.2243	168
	2	115	24	0.012	0.12	23	1691	213.090	0.2281	2.3286	Std Err of Y Est	0.0565	
	3	115	60	0.012	0.12	57.5	29103	283.970	1.4639	2.4533	r <sup>2</sup>	0.9503	
	4	115	120	0.012	0.12	115	81553	334.470	1.9114	2.5244	No. of Observations	4	
		•	•	•	•	•	•	•	•	•	Degrees of Freedom	2	]
											X Coefficient(s)	0.1648	]
											Std Err of Coef.	0.0266	

·		Stock			I								Kd
		Spike Solution	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)		Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
3A 1	L	115	12	0.012	0.12	11.5	51	114.490	-1.2924	2.0588	Constant	2.3654	232
2	2	115	24	0.012	0.12	23	1345	216.550	0.1287	2.3356	Std Err of Y Est	0.0528	
3	3	115	60	0.012	0.12	57.5	11249	462.510	1.0511	2.6651	r <sup>2</sup>	0.9837	1
4	1	115	120	0.012	0.12	115	50169	648.310	1.7004	2.8118	No. of Observations	4	1
				•							Degrees of Freedom	2	1
											X Coefficient(s)	0.2581	1
											Std Err of Coef.	0.0235	1
3B 1	L	115	12	0.012	0.12	11.5	49	114.510	-1.3098	2.0588	Constant	2.3742	237
2	2	115	24	0.012	0.12	23	1128	218.720	0.0523	2.3399	Std Err of Y Est	0.0505	1
3	3	115	60	0.012	0.12	57.5	10093	474.070	1.0040	2.6758	r <sup>2</sup>	0.9847	1
4	1	115	120	0.012	0.12	115	52980	620.200	1.7241	2.7925	No. of Observations	4	
				I.	•	l .	•				Degrees of Freedom	2	1
											X Coefficient(s)	0.2519	1
											Std Err of Coef.	0.0222	1
3C 1	L	115	12	0.012	0.12	11.5	60	114.400	-1.2218	2.0584	Constant	2.3821	241
2	2	115	24	0.012	0.12	23	581	224.190	-0.2358	2.3506	Std Err of Y Est	0.028	1
3	3	115	60	0.012	0.12	57.5	11860	456.400	1.0741	2.6593	r <sup>2</sup>	0.9952	
4	1	115	120	0.012	0.12	115	52980	620.200	1.7241	2.7925	No. of Observations	4	1
		1	1	ı		1					Degrees of Freedom	2	1
											X Coefficient(s)	0.2482	1
											Std Err of Coef.	0.0122	1

Table D-6 (cont.) Day 180 results – K<sub>d</sub> experiments.

Soil	Sample			Tungstat	æ		X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	$K_{d}$
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
4A	1	115	12	0.012	0.12	11.5	636	108.640	-0.1965	2.0360	Constant	2.1426	139
	2	115	24	0.012	0.12	23	3810	191.900	0.5809	2.2831	Std Err of Y Est	0.1651	1
	3	115	60	0.012	0.12	57.5	30252	272.480	1.4808	2.4353	r <sup>2</sup>	0.3428	1
	4	115	120	0.012	0.12	115	99026	159.740	1.9957	2.2034	No. of Observations	4	1
											Degrees of Freedom	2	
											X Coefficient(s)	0.1003	
											Std Err of Coef.	0.0982	
4B	1	115	12	0.012	0.12	11.5	600	109.000	-0.2218	2.0374	Constant	2.097	125
	2	115	24	0.012	0.12	23	5807	171.930	0.7640	2.2354	Std Err of Y Est	0.0653	
	3	115	60	0.012	0.12	57.5	33857	236.430	1.5296	2.3737	r <sup>2</sup>	0.8693	
	4	115	120	0.012	0.12	115	94123	208.770	1.9737	2.3197	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.01429	
											Std Err of Coef.	0.0392	
4C	1	115	12	0.012	0.12	11.5	1065	104.350	0.0273	2.0185	Constant	2.1256	134
	2	115	24	0.012	0.12	23	6022	169.780	0.7797	2.2299	Std Err of Y Est	0.2175	1
	3	115	60	0.012	0.12	57.5	35934	215.660	1.5555	2.3338	r <sup>2</sup>	0.0015	1
	4	115	120	0.012	0.12	115	106000	90.000	2.0253	1.9542	No. of Observations	4	1
			•	•		•	•	-	•	•	Degrees of Freedom	2	1
											X Coefficient(s)	0.0077	
											Std Err of Coef.	0.1429	1

Table D-6 (cont.) Day 180 results – K<sub>d</sub> experiments.

Soil	Sample			Tungstat	e		X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					•
5A	1	115	12	0.012	0.12	11.5	164	113.360	-0.7852	2.0545	Constant	2.5259	336
	2	115	24	0.012	0.12	23	358	226.420	-0.4461	2.3549	Std Err of Y Est	0.0617	
	3	115	60	0.012	0.12	57.5	2481	550.190	0.3946	2.7405	r <sup>2</sup>	0.986	
	4	115	120	0.012	0.12	115	9314	1056.860	0.9691	3.0240	No. of Observations	4	
											Degrees of Freedom	2	
											X Coefficient(s)	0.5307	
											Std Err of Coef.	0.0447	
5B	1	115	12	0.012	0.12	11.5	180	113.200	-0.7447	2.0538	Constant	2.5443	350
	2	115	24	0.012	0.12	23	327	226.730	-0.4855	2.3555	Std Err of Y Est	0.0784	
	3	115	60	0.012	0.12	57.5	2309	551.910	0.3634	2.7419	r <sup>2</sup>	0.9778	
	4	115	120	0.012	0.12	115	7523	1074.770	0.8764	3.0313	No. of Observations	4	
			•								Degrees of Freedom	2	
											X Coefficient(s)	0.5653	
											Std Err of Coef.	0.0603	
5C	1	115	12	0.012	0.12	11.5	150	113.500	-0.8239	2.0550	Constant	2.5273	337
	2	115	24	0.012	0.12	23	339	226.610	-0.4698	2.3553	Std Err of Y Est	0.0704	
	3	115	60	0.012	0.12	57.5	2311	551.890	0.3638	2.7419	r <sup>2</sup>	0.9816	
	4	115	120	0.012	0.12	115	11188	1038.120	1.0488	3.0162	No. of Observations	4	
		•			•		•		•		Degrees of Freedom	2	
											X Coefficient(s)	0.4976	
											Std Err of Coef.	0.0482	

Soil	Sample			Tungsta	te		X axis	Y axis	Log x axis	Log y axis	Regression Ou	tput	Kd
		Stock Spike Solution (mg/L)	Stock Spike Volume (mL)	Soil Mass (kg)	Solution Volume (L)	Spike (mg/L)	Conc. Measured after Equilibrium (ug/L)	Wt. Absorbed (mg)/ Wt. Sorbent (kg)					
6A	1	115	12	0.012	0.12	11.5	39	114.610	-1.4089	2.0592	Constant	2.5694	371
	2	115	24	0.012	0.12	23	206	227.940	-0.6861	2.3578	Std Err of Y Est	0.0411	]
	3	115	60	0.012	0.12	57.5	2506	549.940	0.3990	2.7403	r <sup>2</sup>	0.9932	1
	4	115	120	0.012	0.12	115	19399	956.010	1.2878	2.9805	No. of Observations	4	1
											Degrees of Freedom	2	1
											X Coefficient(s)	0.342	1
											Std Err of Coef.	0.02	
6B	1	115	12	0.012	0.12	11.5	45	114.550	-1.3468	2.0590	Constant	2.514	327
	2	115	24	0.012	0.12	23	300	227.000	-0.5229	2.3560	Std Err of Y Est	0.1054	1
	3	115	60	0.012	0.12	57.5	2265	552.350	0.3551	2.7422	r <sup>2</sup>	0.9492	1
	4	115	120	0.012	0.12	115	34493	805.070	1.5377	2.9058	No. of Observations	4	1
					•						Degrees of Freedom	2	
											X Coefficient(s)	0.3243	1
											Std Err of Coef.	0.0493	1
6C	1	115	12	0.012	0.12	11.5	31	114.690	-1.5086	2.0595	Constant	2.5578	361
	2	115	24	0.012	0.12	23	272	227.280	-0.5654	2.3566	Std Err of Y Est	0.0516	
	3	115	60	0.012	0.12	57.5	2383	551.170	0.3771	2.7413	r <sup>2</sup>	0.989	
	4	115	120	0.012	0.12	115	22891	921.090	1.3597	2.9643	No. of Observations	4	1
											Degrees of Freedom	2	
											X Coefficient(s)	0.3243	1
											Std Err of Coef.	0.0242	1

# **Appendix E. Substrate Effect on Sorption/Desorption Test Results**

## Methodology

In the sorption test, 4.5 g of material was placed into 4-oz amber glass jars for each media type, (see Section 4.4.1.2). Each media type consisted of three replicates. A 70-mL solution containing DI at a concentration of 10 mg/L of sodium tungstate was added to the 4-oz jars. The jars were placed on a shaker table at 100 rpm for 24 hr, removed from the shaker table, and allowed to settle for 2 hr. For some experiments, MMR22S1 soil was utilized, which contained 1,534 mg/kg tungsten. Experiments 25 through 36 used 4.5 g of MMR22S1 soil with a quantity of KPO4 added. After 2 hr, a majority of liquid was removed, filtered, chilled, and sent to EL for analysis. Desorption experiments consisted of drying soil (typically for 1 week) to remove any remaining water from the sorption test. Seventy mL of DI was added to each 4-oz jar, which was then placed on a shaker table at 100 rpm for 24 hr. After shaking, the jars were allowed to settle for 2 hr, and an aliquot of solution was removed, filtered, chilled, and sent to EL for analysis.

## **Discussion**

Note that data presented in this appendix should only be utilized for a qualitative assessment. Significant discrepancies exist between some replicate results (sorption experiment samples 13 through 15 and 31 through 33), and desorption experiment samples (10d through 12d, 15d and 15d dup, 16d through 18d, and 19d through 21d). In addition, all sorption samples were spiked at 10 mg/L, but many results are higher than those for the spiked concentration; this is problematic. Instrument data was reviewed by the analytical laboratory, but no errors were identified. The experimental protocol was also reviewed, and no errors were identified. Regardless, the experiments should be repeated in order to provide a quantitative assessment.

Table E-1. Results of sorption / desorption study.

Sc	orption Te	est	Des	orption <sup>*</sup>	Test	
Sample ID	Rep#	Tungsten (µg/L)	Sample ID	Rep #	Tungsten (µg/L)	Treatment
1	1	107	1d	1	6.54	
2	2	NA	2d	2	3.26	Aluminum Powder
3	3	105	3d	3	<0.02	
4	1	40,600	4d	1	2,290	
5	2	30,900	5d	2	2,760	- Kaolinite - Clay
		NS	5d dup	2	2,820	- Naoimite - Olay
6	3	25,900	6d	3	NA	
7	1	33,400	7d	1	640	
8	2	31,200	8d	2	666	Goethite - Manganese Rich
9	3	36,300	9d	3	632	
10	1	4,190	10d	1	1,750	
11	2	3,590	11d	2	769	Peat - Organic Matter
12	3	3,960	12d	3	1,240	
13	1	8,100	13d	1	506	
14	2	9,090	14d	2	484	- Ottawa Sand
15	3	15,600	15d	3	521	- Ottawa Sanu
15 dup		NS	15d dup	3	<0.02	
16	1	NA	16d	1	7,390	
17	2	37,700	17d	2	10,700	MMR22S1 Cold (7.2°C)
18	3	39,400	18d	3	8,590	
19	1	27,200	19d	1	9,720	
20	2	27,700	20d	2	9,780	MMR22S1 Room Temp
21	3	28,700	21d	3	15,100	
22	1	<0.02	22d	1	NS	
23	2	<0.02	23d	2	NS	DI Blank
24	3	<0.02	24d	3	NS	]
25	1	13,500	25d	1	8,290	
26	2	13,400	26d	2	9,040	MMR22S1 + 1 mg KPO <sub>4</sub>
27	3	14,200	27d	3	9,050	]

NS - no sample; dup - duplicate; NA - not analyzed.

Table E-1 (cont). Results of sorption / desorption study.

So	rption Te	st	Des	sorption 1	Test .	
Sample ID	Rep#	Tungsten (µg/L)	Sample ID	Rep#	Tungsten (µg/L)	Treatment
28	1	13,700	28d	1	9,060	
29	2	13,400	29d	2	8,450	MMR22S1 + 2 mg KPO <sub>4</sub>
30	3	13,900	30d	3	8,640	
31	1	233	31d	1	8,360	
32	2	13,000	32d	2	8,440	MMR22S1 + 4 mg KPO <sub>4</sub>
33	3	13,400	33d	3	11,200	
34	1	12,900	34d	1	10,600	
35	2	13,100	35d	2	8,410	MMR22S1 + 8 mg KPO <sub>4</sub>
36	3	13,100	36d	3	9,020	

NS - no sample; dup - duplicate; NA - not analyzed.

# **Appendix F. Chloride Tracer and Tungsten Results From Column Studies**

Table F-1. Column 1. Chloride tracer test and desorption test. Chloride spiked at 50 mg/L. Initial soil-tungsten concentration is 52 mg/kg.

Vial Number	Start Date and Time	Fill Date and Time	Days Since Previous Sample	Cumm Vol (mL)	Cumm Vol (L)	Pore Volume	Total Elapsed Time (hr)	Effluent W (mg/L)	Effluent Cl (mg/L)
1	5/14/08 15:55	5/14/08 16:20	0.000	0	0	0.00	0.42	NA	0.01
4	5/14/08 17:10	5/14/08 17:35	0.017	22.5	0.02	0.11	1.68	NA	14.52
5	5/14/08 17:35	5/14/08 18:00	0.017	30	0.03	0.15	2.1	0.533	NA
8	5/14/08 18:50	5/14/08 19:15	0.017	52.5	0.05	0.26	3.36	NA	19.795
9	5/14/08 19:15	5/14/08 19:40	0.017	60	0.06	0.29	3.78	0.374	NA
12	5/14/08 20:30	5/14/08 20:55	0.017	82.5	0.08	0.40	5.04	NA	13.459
20	5/14/08 23:50	5/15/08 0:15	0.017	142.5	0.14	0.69	8.4	NA	28.325
24	5/15/08 1:30	5/15/08 1:55	0.017	172.5	0.17	0.84	10.08	NA	34.83
25	5/15/08 1:55	5/15/08 2:20	0.017	180	0.18	0.87	10.5	0.212	NA
28	5/15/08 3:10	5/15/08 3:35	0.017	202.5	0.20	0.98	11.76	NA	37.55
32	5/15/08 4:50	5/15/08 5:15	0.017	232.5	0.23	1.13	13.44	NA	38.75
33	5/15/08 5:15	5/15/08 5:40	0.017	240	0.24	1.17	13.86	0.182	NA
36	5/15/08 6:30	5/15/08 6:55	0.017	262.5	0.26	1.28	15.12	NA	39.55
42	5/15/08 9:00	5/15/08 9:25	0.017	307.5	0.31	1.49	17.64	NA	40.68
43	5/15/08 9:25	5/15/08 9:50	0.017	315	0.31	1.53	18.06	0.175	NA
48	5/15/08 11:30	5/15/08 11:55	0.017	352.5	0.35	1.71	20.16	NA	42.82
51	5/15/08 12:45	5/15/08 13:10	0.017	375	0.37	1.82	21.42	0.171	NA
60	5/15/08 16:30	5/15/08 16:55	0.017	442.5	0.44	2.15	25.2	NA	45.56
61	5/15/08 16:55	5/15/08 17:20	0.017	450	0.45	2.19	25.62	0.172	NA
72	5/15/08 21:30	5/15/08 21:55	0.017	532.5	0.53	2.59	30.24	NA	47.57
73	5/15/08 21:55	5/15/08 22:20	0.017	540	0.54	2.62	30.66	0.164	NA
84	5/16/08 2:30	5/16/08 2:55	0.017	622.5	0.62	3.02	35.28	0.149	NA
96	5/16/08 7:30	5/16/08 7:55	0.017	712.5	0.71	3.46	40.32	NA	48.39
97	5/16/08 7:55	5/16/08 8:20	0.017	720	0.72	3.50	40.74	0.146	NA
108	5/16/08 12:30	5/16/08 12:55	0.017	802.5	0.80	3.90	45.36	NA	48.65
5	5/16/08 15:00	5/16/08 15:30	0.021	847.5	0.85	4.12	47.86	NA	51.96

Cumm – cumulative; NA – not analyzed; Cl – chloride; W – tungsten.

Vial Number	Start Date and Time	Fill Date and Time	Days Since Previous Sample	Cumm Vol (mL)	Cumm Vol (L)	Pore Volume	Total Elapsed Time (hr)	Effluent W (mg/L)	Effluent Cl (mg/L)
7	5/16/08 16:00	5/16/08 16:30	0.021	865.5	0.87	4.20	48.86	0.157	NA
11	5/16/08 18:00	5/16/08 18:30	0.021	901.5	0.90	4.38	50.86	NA	51.43
18	5/16/08 21:30	5/16/08 22:00	0.021	964.5	0.96	4.68	54.36	NA	33.63
27	5/17/08 2:00	5/17/08 2:30	0.021	1045.5	1.05	5.08	58.86	NA	15.488
31	5/17/08 4:00	5/17/08 4:30	0.021	1081.5	1.08	5.25	60.86	0.184	NA
35	5/17/08 6:00	5/17/08 6:30	0.021	1117.5	1.12	5.43	62.86	NA	8.63
42	5/17/08 9:30	5/17/08 10:00	0.021	1180.5	1.18	5.73	66.36	NA	5.32
75	5/18/08 2:00	5/18/08 2:30	0.021	1477.5	1.48	7.18	82.86	NA	0.33
79	5/18/08 4:00	5/18/08 4:30	0.021	1513.5	1.51	7.35	84.86	0.171	NA
87	5/18/08 8:00	5/18/08 8:30	0.021	1585.5	1.59	7.70	88.86	NA	0.24
99	5/18/08 14:00	5/18/08 14:30	0.021	1693.5	1.69	8.23	94.86	NA	0.2
103	5/18/08 16:00	5/18/08 16:30	0.021	1729.5	1.73	8.40	96.86	0.178	NA
123	5/19/08 2:00	5/19/08 2:30	0.021	1909.5	1.91	9.27	106.86	NA	0.2
127	5/19/08 4:00	5/19/08 4:30	0.021	1945.5	1.95	9.45	108.86	0.179	NA
147	5/19/08 14:00	5/19/08 14:30	0.021	2125.5	2.13	10.32	118.86	NA	0.17
151	6/2/08 10:00	6/2/08 10:30	3.767	8101.5	8.10	39.35	450.86	0.143	NA

Cumm – cumulative; NA – not analyzed; Cl – chloride; W – tungsten.

Table F-2. Column 2. Chloride tracer test and tungsten sorption test. Chloride spiked at 50 mg/L. Tungsten spiked at 10 mg/L. Initial soil-tungsten concentration 52 mg/kg.

Vial Number	Start Date and Time	Fill Date and Time	Days Since Previous Sample	Cumm Vol (ml)	Cumm Vol (L)	Pore Volume	Total Elapsed Time (hr)	Effluent W (mg/L)	Effluent Cl (mg/L
1	6/23/08 15:15	6/23/08 15:45	0.0000	0	0	0.00	0	0.688	NA
5	6/23/08 17:45	6/23/08 18:15	0.0208	45	0.045	0.22	2.5	0.496	NA
9	6/23/08 19:45	6/23/08 20:15	0.0208	81	0.081	0.39	4.5	0.431	NA
13	6/23/08 21:45	6/23/08 22:15	0.0208	117	0.117	0.57	6.5	0.394	NA
17	6/23/08 23:45	6/24/08 0:15	0.0208	153	0.153	0.74	8.5	0.402	NA
21	6/24/08 1:45	6/24/08 2:15	0.0208	189	0.189	0.92	10.5	0.372	NA
25	6/24/08 3:45	6/24/08 4:15	0.0208	225	0.225	1.09	12.5	0.357	NA
29	6/24/08 5:45	6/24/08 6:15	0.0208	261	0.261	1.27	14.5	0.355	NA
33	6/24/08 7:45	6/24/08 8:15	0.0208	297	0.297	1.44	16.5	0.344	NA
35	6/24/08 8:45	6/24/08 9:15	0.0208	315	0.315	1.53	17.5	NA	50.35
37	6/24/08 9:45	6/24/08 10:15	0.0208	333	0.333	1.62	18.5	0.337	NA
39	6/24/08 10:45	6/24/08 11:15	0.0208	351	0.351	1.70	19.5	NA	50.09
41	6/24/08 11:45	6/24/08 12:15	0.0208	369	0.369	1.79	20.5	0.316	NA
43	6/24/08 12:45	6/24/08 13:15	0.0208	387	0.387	1.88	21.5	NA	49.85
45	6/24/08 13:45	6/24/08 14:15	0.0208	405	0.405	1.97	22.5	0.308	NA
47	6/24/08 14:45	6/24/08 15:15	0.0208	423	0.423	2.05	23.5	NA	49.46
49	6/24/08 15:45	6/24/08 16:15	0.0208	441	0.441	2.14	24.5	0.323	NA
51	6/24/08 16:45	6/24/08 17:15	0.0208	459	0.459	2.23	25.5	NA	48.98
53	6/24/08 17:45	6/24/08 18:15	0.0208	477	0.477	2.32	26.5	0.306	NA
55	6/24/08 18:45	6/24/08 19:15	0.0208	495	0.495	2.40	27.5	NA	48.77
57	6/24/08 19:45	6/24/08 20:15	0.0208	513	0.513	2.49	28.5	0.28	NA
84	6/25/08 9:15	6/25/08 9:45	0.0208	756	0.756	3.67	42	NA	48.57
86	6/25/08 10:15	6/25/08 10:45	0.0208	774	0.774	3.76	43	0.276	NA
88	6/25/08 11:15	6/25/08 11:45	0.0208	792	0.792	3.85	44	NA	47.35
90	6/25/08 12:15	6/25/08 12:45	0.0208	810	0.81	3.93	45	0.241	NA
92	6/25/08 13:15	6/25/08 13:45	0.0208	828	0.828	4.02	46	NA	48.03
130	6/26/08 8:15	6/26/08 8:45	0.7292	1170	1.17	5.68	65	0.36	NA
131	6/26/08 8:45	6/26/08 9:15	0.0208	1179	1.179	5.73	65.5	NA	NA
132	6/26/08 9:15	6/26/08 9:45	0.0208	1188	1.188	5.77	66	NA	47.15
134	6/26/08 10:15	6/26/08 10:45	0.0208	1206	1.206	5.86	67	0.361	NA
136	6/26/08 11:15	6/26/08 11:45	0.0208	1224	1.224	5.95	68	NA	48.88
138	6/26/08 12:15	6/26/08 12:45	0.0208	1242	1.242	6.03	69	0.403	NA
140	6/26/08 13:15	6/26/08 13:45	0.0208	1260	1.26	6.12	70	NA	46.89
143	6/26/08 14:45	6/26/08 15:15	0.0208	1287	1.287	6.25	71.5	0.38	NA
145	6/26/08 15:45	6/26/08 16:15	0.0208	1305	1.305	6.34	72.5	NA	47.22
147	6/26/08 16:45	6/26/08 17:15	0.0208	1323	1.323	6.43	73.5	0.373	NA

Vial Number	Start Date and Time	Fill Date and Time	Days Since Previous Sample	Cumm Vol	Cumm Vol (L)	Pore Volume	Total Elapsed Time (hr)	Effluent W (mg/L)	Effluent Cl (mg/L
149	6/26/08 17:45	6/26/08 18:15	0.0208	1341	1.341	6.51	74.5	NA	47.27
151	6/26/08 18:45	6/26/08 19:15	0.0208	1359	1.359	6.60	75.5	0.364	NA
153	6/26/08 19:45	6/26/08 20:15	0.0208	1377	1.377	6.69	76.5	NA	46.93
155	6/26/08 20:45	6/26/08 21:15	0.0208	1395	1.395	6.78	77.5	0.358	NA
157	6/26/08 21:45	6/26/08 22:15	0.0208	1413	1.413	6.86	78.5	NA	47.38
159	6/26/08 22:45	6/26/08 23:15	0.0208	1431	1.431	6.95	79.5	0.346	NA
160	6/26/08 23:15	6/26/08 23:45	0.0208	1440	1.44	6.99	80	NA	NA
161	6/26/08 23:45	6/27/08 0:15	0.0208	1449	1.449	7.04	80.5	NA	46.57
163	6/27/08 0:45	6/27/08 1:15	0.0208	1467	1.467	7.13	81.5	0.333	NA
165	6/27/08 1:45	6/27/08 2:15	0.0208	1485	1.485	7.21	82.5	NA	47.26
167	6/27/08 2:45	6/27/08 3:15	0.0208	1503	1.503	7.30	83.5	0.313	NA
169	6/27/08 3:45	6/27/08 4:15	0.0208	1521	1.521	7.39	84.5	NA	47.98
171	6/27/08 4:45	6/27/08 5:15	0.0208	1539	1.539	7.48	85.5	0.315	NA
173	6/27/08 5:45	6/27/08 6:15	0.0208	1557	1.557	7.56	86.5	NA	47.9
177	6/27/08 7:45	6/27/08 8:15	0.0208	1593	1.593	7.74	88.5	0.317	NA
178	6/27/08 8:15	6/27/08 8:45	0.0208	1602	1.602	7.78	89	NA	NA
179	6/27/08 8:45	6/27/08 9:15	0.0208	1611	1.611	7.82	89.5	NA	48.87
180	6/27/08 9:15	6/27/08 9:45	0.0208	1620	1.62	7.87	90	NA	NA
181	6/27/08 9:45	6/27/08 10:15	0.0208	1629	1.629	7.91	90.5	0.32	NA
183	6/27/08 10:45	6/27/08 11:15	0.0208	1647	1.647	8.00	91.5	NA	48.13
185	6/27/08 11:45	6/27/08 12:15	0.0208	1665	1.665	8.09	92.5	0.32	NA
186	6/27/08 12:15	6/27/08 12:45	0.0208	1674	1.674	8.13	93	NA	NA
187	6/27/08 12:45	6/27/08 13:15	0.0208	1683	1.683	8.17	93.5	NA	49.59
189	6/27/08 13:45	6/27/08 14:15	0.0208	1701	1.701	8.26	94.5	0.333	NA
191	6/27/08 14:45	6/27/08 15:15	0.0208	1719	1.719	8.35	95.5	NA	49.28
193	6/27/08 15:45	6/27/08 16:15	0.0208	1737	1.737	8.44	96.5	0.378	NA
195	6/27/08 16:45	6/27/08 17:15	0.0208	1755	1.755	8.52	97.5	NA	33.54
197	6/27/08 17:45	6/27/08 18:15	0.0208	1773	1.773	8.61	98.5	0.432	NA
199	6/27/08 18:45	6/27/08 19:15	0.0208	1791	1.791	8.70	99.5	NA	18.39
201	6/27/08 19:45	6/27/08 20:15	0.0208	1809	1.809	8.79	100.5	0.443	NA
203	6/27/08 20:45	6/27/08 21:15	0.0208	1827	1.827	8.87	101.5	NA	9.57
205	6/27/08 21:45	6/27/08 22:15	0.0208	1845	1.845	8.96	102.5	0.453	NA
207	6/27/08 22:45	6/27/08 23:15	0.0208	1863	1.863	9.05	103.5	NA	5.638
209	6/27/08 23:45	6/28/08 0:15	0.0208	1881	1.881	9.14	104.5	0.436	NA
211	6/28/08 0:45	6/28/08 1:15	0.0208	1899	1.899	9.22	105.5	NA	4.386
213	6/28/08 1:45	6/28/08 2:15	0.0208	1917	1.917	9.31	106.5	0.432	NA
215	6/28/08 2:45	6/28/08 3:15	0.0208	1935	1.935	9.40	107.5	NA	4.055
217	6/28/08 3:45	6/28/08 4:15	0.0208	1953	1.953	9.49	108.5	0.426	NA

Vial Number	Start Date and Time	Fill Date and Time	Days Since Previous Sample	Cumm Vol (ml)	Cumm Vol (L)	Pore Volume	Total Elapsed Time (hr)	Effluent W (mg/L)	Effluent Cl (mg/L
219	6/28/08 4:45	6/28/08 5:15	0.0208	1971	1.971	9.57	109.5	NA	3.917
221	6/28/08 5:45	6/28/08 6:15	0.0208	1989	1.989	9.66	110.5	0.406	NA
223	6/28/08 6:45	6/28/08 7:15	0.0208	2007	2.007	9.75	111.5	NA	3.689
226	6/28/08 8:15	6/28/08 8:45	0.0208	2034	2.034	9.88	113	0.392	NA
228	6/28/08 9:15	6/28/08 9:45	0.0208	2052	2.052	9.97	114	NA	3.416
230	6/28/08 10:15	6/28/08 10:45	0.0208	2070	2.07	10.05	115	0.383	NA
232	6/28/08 11:15	6/28/08 11:45	0.0208	2088	2.088	10.14	116	NA	2.958
234	6/28/08 12:15	6/28/08 12:45	0.0208	2106	2.106	10.23	117	0.381	NA
236	6/28/08 13:15	6/28/08 13:45	0.0208	2124	2.124	10.32	118	NA	2.337
238	6/28/08 14:15	6/28/08 14:45	0.0208	2142	2.142	10.40	119	0.37	NA
240	6/28/08 15:15	6/28/08 15:45	0.0208	2160	2.16	10.49	120	NA	1.645
242	6/28/08 16:15	6/28/08 16:45	0.0208	2178	2.178	10.58	121	0.35	NA
244	6/28/08 17:15	6/28/08 17:45	0.0208	2196	2.196	10.67	122	NA	1.237
246	6/28/08 18:15	6/28/08 18:45	0.0208	2214	2.214	10.75	123	0.369	NA
247	6/28/08 18:45	6/28/08 19:15	0.0208	2223	2.223	10.80	123.5	NA	0.947

Cumm – cumulative; NA – not analyzed; Cl – chloride; W – tungsten.

Table F-3. Column 3. 1, Chloride tracer test and desorption test. Chloride spiked at 50 mg/L. Soil was 50:50 mixture of samples containing 52 mg/kg and 28 mg/kg of tungsten.

Vial Number  0 2 4 6	7/9/08 14:45 7/9/08 15:15 7/9/08 15:45 7/9/08 16:15 7/9/08 16:45 7/9/08 17:15 7/9/08 17:45	Fill Date and Time  7/9/08 15:00  7/9/08 15:30  7/9/08 16:00  7/9/08 16:30  7/9/08 17:00  7/9/08 17:30	0.0104 0.0104 0.0104 0.0104	0 9 18 27	0.009 0.018	Pore Volume 0.00 0.04 0.09	Time (hr) 0 0.50	W (mg/L) NA 0.697	CI (mg/L) 0.01
2 4 6	7/9/08 15:15 7/9/08 15:45 7/9/08 16:15 7/9/08 16:45 7/9/08 17:15	7/9/08 15:30 7/9/08 16:00 7/9/08 16:30 7/9/08 17:00	0.0104 0.0104 0.0104	9 18	0.009	0.04	0.50		
4 6	7/9/08 15:45 7/9/08 16:15 7/9/08 16:45 7/9/08 17:15	7/9/08 16:00 7/9/08 16:30 7/9/08 17:00	0.0104 0.0104 0.0104	18				0.697	NA
6	7/9/08 16:15 7/9/08 16:45 7/9/08 17:15	7/9/08 16:30 7/9/08 17:00	0.0104 0.0104		0.018	0.09			1
	7/9/08 16:45 7/9/08 17:15	7/9/08 17:00	0.0104	27			1.00	NA	12.669
8	7/9/08 17:15	, ,			0.027	0.13	1.50	0.617	NA
_		7/9/08 17:30		36	0.036	0.17	2.00	NA	19.4614
10	7/9/08 17:45		0.0104	45	0.045	0.22	2.50	0.556	NA
12		7/9/08 18:00	0.0104	54	0.054	0.26	3.00	NA	22.3914
15	7/9/08 18:30	7/9/08 18:45	0.0104	67	0.0675	0.33	3.75	0.53	NA
17	7/9/08 19:00	7/9/08 19:15	0.0104	76	0.0765	0.37	4.25	NA	29.7718
19	7/9/08 19:30	7/9/08 19:45	0.0104	85	0.0855	0.42	4.75	0.519	NA
21	7/9/08 20:00	7/9/08 20:15	0.0104	94	0.0945	0.46	5.25	NA	33.8527
23	7/9/08 20:30	7/9/08 20:45	0.0104	103	0.1035	0.50	5.75	0.503	NA
25	7/9/08 21:00	7/9/08 21:15	0.0104	112	0.1125	0.55	6.25	NA	35.4914
27	7/9/08 21:30	7/9/08 21:45	0.0104	121	0.1215	0.59	6.75	0.491	NA
29	7/9/08 22:00	7/9/08 22:15	0.0104	130	0.1305	0.63	7.25	NA	36.6388
31	7/9/08 22:30	7/9/08 22:45	0.0104	139	0.1395	0.68	7.75	0.484	NA
33	7/9/08 23:00	7/9/08 23:15	0.0104	148	0.1485	0.72	8.25	NA	37.1094
35	7/9/08 23:30	7/9/08 23:45	0.0104	157	0.1575	0.77	8.75	0.479	NA
37	7/10/08 0:00	7/10/08 0:15	0.0104	166	0.1665	0.81	9.25	NA	39.9926
39	7/10/08 0:30	7/10/08 0:45	0.0104	175	0.1755	0.85	9.75	0.464	NA
41	7/10/08 1:00	7/10/08 1:15	0.0104	184	0.1845	0.90	10.25	NA	41.1446
43	7/10/08 1:30	7/10/08 1:45	0.0104	193	0.1935	0.94	10.75	0.458	NA
45	7/10/08 2:00	7/10/08 2:15	0.0104	202	0.2025	0.98	11.25	NA	42.6534
47	7/10/08 2:30	7/10/08 2:45	0.0104	211	0.2115	1.03	11.75	0.447	NA
50	7/10/08 3:15	7/10/08 3:30	0.0104	225	0.225	1.09	12.50	NA	43.3697
55	7/10/08 4:30	7/10/08 4:45	0.0104	247	0.2475	1.20	13.75	0.438	NA
57	7/10/08 5:00	7/10/08 5:15	0.0104	256	0.2565	1.25	14.25	NA	44.0877
63	7/10/08 6:30	7/10/08 6:45	0.0104	283	0.2835	1.38	15.75	0.43	NA
65	7/10/08 7:00	7/10/08 7:15	0.0104	292	0.2925	1.42	16.25	NA	42.0708
73	7/10/08 9:00	7/10/08 9:15	0.0104	328	0.3285	1.60	18.25	0.421	NA

Vial Number	Start Date and Time	Fill Date and Time	Days Since Previous Sample	Cumm Vol (ml)	Cumm Vol (L)	Pore Volume	Total Elapsed Time (hr)	Effluent W (mg/L)	Effluent Cl (mg/L)
75	7/10/08 9:30	7/10/08 9:45	0.0104	337	0.3375	1.64	18.75	NA	45.3294
81	7/10/08 11:00	7/10/08 11:15	0.0104	364	0.3645	1.77	20.25	0.433	NA
83	7/10/08 11:30	7/10/08 11:45	0.0104	373	0.3735	1.81	20.75	NA	45.1753
89	7/10/08 13:00	7/10/08 13:15	0.0104	400	0.4005	1.95	22.25	0.431	NA
91	7/10/08 13:30	7/10/08 13:45	0.0104	409	0.4095	1.99	22.75	NA	46.0505
97	7/10/08 15:00	7/10/08 15:15	0.0104	436	0.4365	2.12	24.25	0.436	NA
99	7/10/08 15:30	7/10/08 15:45	0.0104	445	0.4455	2.16	24.75	NA	47.0253
100	7/10/08 15:45	7/10/08 16:00	0.0104	450	0.45	2.19	25.00	0.435	NA
102	7/10/08 16:15	7/10/08 16:30	0.0104	459	0.459	2.23	25.50	NA	48.3484
104	7/10/08 16:45	7/10/08 17:00	0.0104	468	0.468	2.27	26.00	0.457	NA
106	7/10/08 17:15	7/10/08 17:30	0.0104	477	0.477	2.32	26.50	NA	35.6103
108	7/10/08 17:45	7/10/08 18:00	0.0104	486	0.486	2.36	27.00	0.528	NA
110	7/10/08 18:15	7/10/08 18:30	0.0104	495	0.495	2.40	27.50	NA	25.2802
112	7/10/08 18:45	7/10/08 19:00	0.0104	504	0.504	2.45	28.00	0.518	NA
114	7/10/08 19:15	7/10/08 19:30	0.0104	513	0.513	2.49	28.50	NA	19.8976
116	7/10/08 19:45	7/10/08 20:00	0.0104	522	0.522	2.54	29.00	0.529	NA
118	7/10/08 20:15	7/10/08 20:30	0.0104	531	0.531	2.58	29.50	NA	15.7554
120	7/10/08 20:45	7/10/08 21:00	0.0104	540	0.54	2.62	30.00	0.551	NA
122	7/10/08 21:15	7/10/08 21:30	0.0104	549	0.549	2.67	30.50	NA	12.9722
124	7/10/08 21:45	7/10/08 22:00	0.0104	558	0.558	2.71	31.00	0.562	NA
126	7/10/08 22:15	7/10/08 22:30	0.0104	567	0.567	2.75	31.50	NA	11.4166
128	7/10/08 22:45	7/10/08 23:00	0.0104	576	0.576	2.80	32.00	0.58	NA
130	7/10/08 23:15	7/10/08 23:30	0.0104	585	0.585	2.84	32.50	NA	10.0901
132	7/10/08 23:45	7/11/08 0:00	0.0104	594	0.594	2.89	33.00	0.577	NA
134	7/11/08 0:15	7/11/08 0:30	0.0104	603	0.603	2.93	33.50	NA	8.6739
136	7/11/08 0:45	7/11/08 1:00	0.0104	612	0.612	2.97	34.00	0.585	NA
138	7/11/08 1:15	7/11/08 1:30	0.0104	621	0.621	3.02	34.50	NA	7.5205
140	7/11/08 1:45	7/11/08 2:00	0.0104	630	0.63	3.06	35.00	0.584	NA
142	7/11/08 2:15	7/11/08 2:30	0.0104	639	0.639	3.10	35.50	NA	6.7259
145	7/11/08 3:00	7/11/08 3:15	0.0104	652	0.6525	3.17	36.25	0.572	NA
147	7/11/08 3:30	7/11/08 3:45	0.0104	661	0.6615	3.21	36.75	NA	5.6594
149	7/11/08 4:00	7/11/08 4:15	0.0104	670	0.6705	3.26	37.25	0.558	NA

Vial Number	Start Date and Time	Fill Date and Time	Days Since Previous Sample	Cumm Vol (ml)	Cumm Vol (L)	Pore Volume	Total Elapsed Time (hr)	Effluent W (mg/L)	Effluent Cl (mg/L)
151	7/11/08 4:30	7/11/08 4:45	0.0104	679	0.6795	3.30	37.75	NA	4.7604
157	7/11/08 6:00	7/11/08 6:15	0.0104	706	0.7065	3.43	39.25	0.549	NA
159	7/11/08 6:30	7/11/08 6:45	0.0104	715	0.7155	3.48	39.75	NA	3.5911
165	7/11/08 8:00	7/11/08 8:15	0.0104	742	0.7425	3.61	41.25	0.533	NA
167	7/11/08 8:30	7/11/08 8:45	0.0104	751	0.7515	3.65	41.75	NA	2.5585
175	7/11/08 10:30	7/11/08 10:45	0.0104	787	0.7875	3.83	43.75	NA	1.5511
177	7/11/08 11:00	7/11/08 11:15	0.0104	796	0.7965	3.87	44.25	0.515	NA
181	7/11/08 12:00	7/11/08 12:15	0.0104	814	0.8145	3.96	45.25	0.507	NA
183	7/11/08 12:30	7/11/08 12:45	0.0104	823	0.8235	4.00	45.75	NA	0.7757
189	7/11/08 14:00	7/11/08 14:15	0.0104	850	0.8505	4.13	47.25	0.483	NA
191	7/11/08 14:30	7/11/08 14:45	0.0104	859	0.8595	4.17	47.75	NA	0.4942
197	7/11/08 16:00	7/11/08 16:15	0.0104	886	0.8865	4.31	49.25	0.466	NA
199	7/11/08 16:30	7/11/08 16:45	0.0104	895	0.8955	4.35	49.75	NA	0.4466

Cumm – cumulative; NA – not analyzed; Cl – chloride; W – tungsten.

## **Appendix G. Unsaturated Zone Modeling Details**

## Introduction

SESOIL is a seasonal compartment model that simulates long-term pollutant fate and migration in the unsaturated zone. The purpose of this modeling is to determine if tungsten will eventually reach groundwater, and if so, at what concentration. SESOIL accounts for:

- Hydrologic processes in the unsaturated soil zone
- Pollutant concentrations and masses in water, soil, and air phases
- Pollutant migration to groundwater
- Pollutant volatilization at the ground surface.

SESOIL estimates the effects of these processes on a monthly basis during the simulation period. The modeled soil column may be composed of up to four layers; each layer has different soil properties that affect the pollutant fate. In addition, each soil layer may be subdivided into a maximum of 10 sub-layers in order to provide enhanced resolution of pollutant fate and migration in the soil column. The model can also account for the following pollutant fate processes: volatilization; adsorption; cation exchange; biodegradation; hydrolysis; and complexation.

SESOIL has been widely used as a screening tool in performing exposure assessments. A number of studies have been conducted on the SESOIL model, including sensitivity analysis, comparison with other models, and comparisons with field data. SESOIL has been used previously at MMR for fate-and-transport analysis of contaminants in the unsaturated zone and soil clean up-level determination (AFCEE 2003; AMEC 2006). This model has also been used to help in refining site-conceptual models and defining future risks to groundwater (AFCEE 2003).

## Site-specific model set up and input parameters

SESOIL requires four sets of input data files as listed below:

 Climate data: consist of monthly rainfall and climatic statistics for a typical year, based on a specific meteorological station of interest

- Soil data: consist of soil parameters such as bulk density and effective porosity
- Chemical data: consist of chemical-specific parameters such as molecular weight, solubility, partitioning coefficients ( $K_{oc}$ ), air and water diffusion coefficients
- Application input: describes compartment specifications, characteristics of pollutant loadings, thickness of soil layers, and additional soil properties beyond those specified in the soil input file (e.g., pH). Vertical variation in soil properties are established for lower layers, as a ratio of the information contained in the soil and chemical files that apply to the uppermost layer.

Specific data and sources for each input file are explained below; tables with input data have been presented by AMEC (2001).

#### Climate data

The weather station closest to Camp Edwards in the SESOIL database is the Hyannis weather station, which is located east of MMR. The database contains mean monthly data on precipitation and temperature, frequency and length of storms, cloud-cover fraction, and relative humidity. Default data from the Hyannis weather station were used except for precipitation. The mean monthly precipitation data acquired between 1976 and 2000 from the MMR weather station were used in the model.

#### Soil data

Soil data required by SESOIL includes bulk density, intrinsic permeability, soil pore disconnectedness index, effective porosity, and organic carbon content. Soil values are based on data collected at Demolition Area 1 at Camp Edwards as part of a column study (bulk density and soil porosity) conducted by the University of Texas (Speitel et al. 2002). For example, the soil-pore disconnectedness index was used as a variable within given constraints in order to obtain the approximate amount of groundwater recharge of 27 in.

Bulk density, intrinsic permeability, and effective porosity are all interrelated parameters. The analysis of soil sample data collected during previous MMR investigations (AFCEE 1998) indicates particle density of the soil matrix is approximately 2.65 g/cm $^3$ . Using a total porosity of 0.42 (AMEC 2005; Speitel et al. 2002), the bulk density (soil-matrix density multiplied by total porosity) is approximately 1.5 g/cm $^3$ . The general range for soil bulk density of sand is 1.18 to 1.58 g/cm $^3$  (Bonazountas and Wagner 1984).

Porosity was measured as part of column studies conducted on Central Impact Area soils by the University of Texas (Speitel et al. 2002). This value, which averaged approximately 42% (0.42) for surficial and subsurface soils, was used for all SESOIL simulations.

Soil intrinsic permeability and the soil pore disconnectedness index are model input parameters, which are not measurable in the field, but both can be estimated. Soil intrinsic permeability can be approximated by multiplying hydraulic conductivity by  $1 \times 10^{-5}$  cm s (centimeter s) (Bonazountas and Wagner 1984). A value of  $5.0 \times 10^{-9}$  cm<sup>2</sup> was used in this model. The soil-pore disconnectedness index relates the soil permeability to soil moisture content, and values typically range from 3.7 for sand to 12.0 for fine clay (Bonazountas and Wagner 1984). A value of 3.9 was used in this model.

Total organic carbon soil data collected from the Demo 1 project area were used to derive a specific value for percent organic carbon in the vadose zone. A value of 1.05% was estimated for the upper layer (0- to 1-ft bgs) from an average of organic carbon samples collected from this depth. This value is consistent with other areas of MMR. An organic carbon value of 0.34% of the surface value was used for the layer between 1- and 10-ft deep. Organic carbon values of 0.1 and 0.013% of the surface value were used for the two lower layers (10-80 ft) and (10-80 ft) respectively, based on data collected at the Demo 1 area.

## **Chemical property data**

Chemical property data used were the same as those used in previous SESOIL modeling efforts and were generally based on data obtained from the USEPA (1996) and RAIS database (ORNL 2005).

## **Application input**

SESOIL allows a multi-layer soil column set up to model the contaminant movement throughout the unsaturated zone. Level of discretization is based on the modeling objective and thickness of the unsaturated zone.

A  $19.8 \times 10.7$ -m grid was used in this analysis. A depth to groundwater of 27 meters was used for the simulation. All four available model layers were used to represent the vertical stratigraphy. The upper layer (Layer 1) was 30.5-cm deep (equivalent to 1 ft) and divided into four sub-layers. The remaining soil column extending to the groundwater table was split into three layers (Layers 2, 3 and 4) of 300 cm, 2100 cm and 305 cm (10,69, and 10 ft) respectively. The three lower layers used the maximum available number of sub-layers (10) in the model to describe the movement of contaminants in the unsaturated zone. The tungsten source is applied in Layer 1 as a one-time release, because training has been discontinued with tungsten ammunition. Thus, the mass in the source will deplete as a result of chemical processes and vertical dispersion as the contaminant migrates through the vadose zone.

## Modeling calibration and sensitivity analysis

In this model, potential contaminants can only migrate to groundwater through the unsaturated zone by dissolving in the recharging water. Thus, recharge rate is a critical factor in the SESOIL model. SESOIL simulates hydrologic parameters (including recharge rate) and transport parameters of a contaminant in the unsaturated zone. Thus, model calibration is necessary for determination of a reasonable site-specific recharge rate so that fate-and-transport of a contaminant can be properly simulated.

Extensive model calibrations were conducted previously through a series of simulations that used various measured versus modeled values of moisture content and recharge rate with depth (AMEC 2005). Because this study used the same soil and meteorological parameters, the model required no further calibration. Using previously described climatic data and soil parameters, the following hydraulic parameters are predicted:

0	Precipitation	118.03 cm
0	Evapotranspiration	46.53 cm
0	Surface runoff	0.03 cm

o Recharge to groundwater 71.49 cm

Average soil moisture content

in source zone 11.37%

Average soil moisture content

below source zone 11.37%

Results are in general agreement with the MMR site conceptual model and field data in western Cape Cod and are consistent with the modeling results conducted by USEPA/INL for the Tango Range [recharge rate of 27 in. per year (68.58 cm/year) and a calibrated soil moisture content of 12.3%]. Thus, detailed model calibrations were not performed.

## AT123D model

The AT123D groundwater transport model (SEVIEW version 6.3; Environmental Software Consultants 2006) was used to predict groundwater concentrations downgradient of the source term. AT123D is a three-dimensional groundwater model developed by G. T. Yeh (1981) at Oak Ridge National Laboratory. Significant modifications were made by researchers (Schneiker 2006). This model can simulate advection, dispersion, sorption, decay, and biodegradation with results used to estimate the distance a contaminant will migrate for specific time periods and locations. Biodegradation was not used in this analysis to allow consistency with other IAGWSP investigations.

#### Site specific model set up and input parameters

AT123D requires two sets of input files; Aquifer and Source Release/Chemical Input Parameters. AT123D aquifer parameters contain information describing soil characteristics and aquifer geometry whereas AT123D input parameters contain information describing the geometry of the source release and contaminant properties. Because SEVIEW software links SESOIL to AT123D, the mass flux of the contaminant is transferred to the input load file in AT123D, as are other parameters specified in SESOIL.

## Aquifer parameters

Effective porosity and soil bulk-density parameters are identical to the values used in the SESOIL model and were discussed previously. The

Demo 1 value of 3.68 m/hr, equivalent to 8,832 cm/day, was used for hydraulic conductivity, and specific gradients were scaled from maps and based on the sub-regional numerical model developed for the Demo 1 site.

Longitudinal, transverse, and vertical dispersivities were specified as 10.00, 2.0, and 0.0116 m, respectively. These values were recommended by USEPA/INL in the Tango range investigation.

The aquifer width and depth were set at infinity per modeling document guidance to provide an easier analytical solution. Because the aquifer boundaries are relatively large in relation to size of the source area, an infinite aquifer along the x and y directions is appropriate (Schneiker 2006).

## Input parameters

The input parameters contain information describing the geometry of the source release and contaminant properties. The source term was oriented with the width (y axis) centered on the sample location and the length (x axis) parallel to groundwater flow. This configuration frames the starting and ending points of the release with the center of the downgradient edge oriented at 0,0. Thus, the four corners of the release area are designated (-x, y/2), (0, y/2), (0, -y/2) and (-x, -y/2), with a centerline defined as (0,0). A mixing zone depth of 3 m was used to provide mixing of contaminants with underlying groundwater.

The remaining chemical inputs are carried over from SESOIL and include organic carbon content, chemical distribution coefficient, and water diffusion coefficient.

## Modeling calibration and sensitivity analysis

Model calibrations were conducted comparing AT123D with numerical transport codes that have been used repetitively at MMR (USGS MODFLOW code; McDonald and Harbaugh 1988). Analyses indicate that AT123D provides acceptable results comparable to numerical transport codes (Cain 2006). AT123D is more conservative in calculating contaminant concentration at the boundary because, unlike numerical transport codes, AT123D does not take into consideration the additional dilution from soil moisture recharge downgradient of the source area.

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## **REPORT DOCUMENTATION PAGE**

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#### 13. SUPPLEMENTARY NOTES

#### 14. ABSTRACT

Batch and column laboratory studies performed tungsten metal in contact with water readily releases dissolved species, and soil partition coefficients ( $K_d$ ) do not stabilize in batch studies for 30 to 60 days. The  $K_d$  values are highly variable, range from 18 to 477 L/kg, and are dependent upon the length of contact time. The rate of dissolution from a tungsten particle appears to range from 0.022 to 0.067 mg/day. These findings indicate metallic tungsten and tungsten oxides are rapidly dissolved under high-intensity precipitation events and are transmitted through the vadose zone soils as tungstate and polytungstate species. If tungstate reaches groundwater, it will continue to be adsorbed by the aquifer matrix, resulting in limited migration from the source area. Polytungstate migration is seemingly attenuated by adsorption processes that prevent it from reaching groundwater.

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